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ETHYLENE POLYMERIZATION PROCESS

FIELD OF THE INVENTION

This invention pertains to a polymerization process for making ethylene polymers characterized as having low or no gels, especially those due to extraneous high molecular

5   weight polymer fractions.

BACKGROUND OF THE INVENTION

Polymerization processes that utilize Ziegler-Natta catalyst or chromium catalyst systems to manufacture ethylene polymers are well known in the art. With the introduction of new metallocene or single-site catalysts, these new catalysts are increasingly used to

10   manufacture ethylene polymers via polymerization, such as gas phase or slurry polymerization processes. Polymerization experience with metallocene or single-site catalyst systems, when used in the same process equipment/configuration as with Ziegler-Natta catalysts or chromium catalysts) indicates that the new catalyst systems characteristically produce polymers with higher gel levels than Ziegler-Natta catalysts.

15   Gels that are observable in ethylene polymers are principally high molecular weight (HMW) polymer chains or fractions that are immiscible with the bulk polymer phase. While a few applications can tolerate gels, for the vast majority of polyethylene applications, gels are undesirable aesthetically or they adversely affect product performance.

It is known that polyethylene as produced still contains active catalyst residues. If the

20   catalyst residues are not promptly deactivated, gels and/or extraneous HMW polymer fractions will result. As a result, catalyst kill agents (e.g. water, O_2, CO and CO_2) are routinely added to the polymer post-reactor in a process-finishing step.

Also, ethylene polymerization typically involves the use of chain terminating agents (e.g. hydrogen and isobutane) to control the product melt index or molecular weight to target.

25   High levels of these agents reduce the molecular weight of the growing polymer by terminating chain growth or propagation. In practice, these agents are injected directly into the reactor wherein their levels are precisely controlled. But chain terminator concentration is not controlled to a high level in post-reactor equipment and vessels, as downstream of the reactor, polyethylene producers routinely vent these agents or at least do not maintain the

30   higher levels previously existent in the reactor.

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In addition to being more prone to providing polymers with higher gel levels and/or higher quantities of extraneous HMW fractions, the use of metallocene or single-site catalysts have been found to result in substantially lower runtimes before the onset of reactor fouling and sheeting. Fouling and sheeting exists as polymer coatings on the reactor wall and internal parts (e.g. stirrer blades and thermocouples). After the onset of fouling and sheeting, and as they continue to buildup, process efficiencies (e.g. catalyst efficiency, product yield and heat transfer) proportionally decrease which can cause a spiral or exponential effect. As fouling and sheeting continue, process efficiencies decrease until such time as continuing the polymerization becomes economically impractical and/or there is gross loss of process control and the ability to produce products that are on-target.

While new forms of catalysts, such as the supported catalyst systems, offer marked improvement in runtime before the onset of fouling and sheeting, additional improvements are needed.

Further, given the wide availability of the new catalysts, ethylene polymer producers desire the ability to use Ziegler-Natta catalysts or chromium catalysts in combination with metallocene or single-site catalysts in the same manufacturing facility to make different polymer products. Producers also desire the flexibility to use the different catalysts simultaneously for a single polymer product such as in a tandem polymerization with a different catalyst system being separately injected into different reactors. But experience indicates that for facilities that utilize both catalyst systems even short runtimes before the onset of fouling and sheeting result relative to an equivalent facility dedicated exclusively to using new catalysts.

Accordingly, there is a need for a polymerization process that utilizes Ziegler-Natta and metallocene or single-site catalysts, either interchangeably or simultaneously, and produces ethylene polymers characterized by reduced gel levels. There is also a need for a polymerization process that utilizes Ziegler-Natta and metallocene or single-site catalysts (either interchangeably or simultaneously), and exhibits improved runtimes before the onset of reactor fouling and sheeting.

SUMMARY OF THE INVENTION

The aforementioned needs are met by one or more aspects of the invention. In one aspect, the invention relates to a polymerization process for making a polymer, the polymer

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comprising ethylene and characterized as having low levels of gels or extraneous high molecular weight (HMW) polymer fractions or both, and the process comprising:

(I)   providing a polymerization system comprising:

    (a)   at least one by-passable purification unit,

5   (b)   at least one catalyst feed vessel,

    (c)   at least one reactor, and

    (d)   post-reactor equipment and vessels, and

(II)   continuously polymerizing ethylene in the at least one reactor in the presence of an active catalyst which is continuously fed to the reactor, continuously

10 transferring the polymerized ethylene downstream through to the post-reactor part of the system and:

    (a)   providing and maintaining a molar ratio of chain terminator to ethylene of from about 0.001 to about 0.5 throughout the post-reactor part of the polymerization system until all active catalyst is deactivated, or

15   (b)   purifying the ethylene by directing the ethylene through the at least one purification unit before entry into the at least one reactor, or

    (c)   providing critically clean catalyst feed vessels

Additional aspects of the invention and advantages provided by various embodiments of the invention will become apparent with the following description.

20   BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a slurry polymerization reactor system used in one embodiment of the invention.

FIG. 2A and FIG. 2B are schematics of feed gas purification systems used in embodiments of the invention.

25   FIG. 3 are photos showing the extent of reactor fouling and/or sheeting for various examples: 3A – Inventive Example 2; 3B – Inventive Example 3; 3C – Comparative Run 2A; and 3D – Comparative Run 2B.

FIG. 4 is a graph of the heat exchange coefficient across the reactor wall (U' values) vs. run time for various levels of ethylene purity.

30   FIG. 5 is a another graph of U' values vs. run time for various levels of ethylene purity.

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DETAILED DESCRIPTION OF THE INVENTION

Embodiments of the invention are based, in part, on one or more of the following discoveries. It has been found that polymerization that utilize metallocene or single-site catalyst systems possesses unique characteristics not typically known for Ziegler-Natta

5   catalysts. Specifically, the chain terminator consumption rate is substantially higher for some metallocene or single-site catalysts relative to Ziegler-Natta catalysts. With regard to reactor fouling and sheeting, some metallocene or single-site catalysts are more sensitive to ethylene feed gas purity levels than Ziegler-Natta catalysts. It has been discovered that gels and/or extraneous HMW fractions can result from mixed catalyst systems due to cross-

10   contamination.

Accordingly, a new polymerization process and a process system are provided. The process system comprises at least one catalyst feed vessel, at least one reactor, and post-reactor equipment and vessels. Optionally, at least one by-passable purification unit is also part of the process system. The polymerization process comprises (a) feeding the reactants

15   and catalysts to the polymerization system; (b) continuously polymerizing monomers or comonomers (such as ethylene and 1-octene) in the reactor in the presence of an active catalyst which is continuously fed to the reactor; and (c) continuously transferring the polymer downstream to the post-reactor vessels. In addition, one or more of the following steps or acts are performed as desired: (1) providing a chain terminator in the post-reactor

20   and maintaining a molar ratio of chain terminator to monomer or comonomer from about 0.001 to about 0.5 in the post-reactor until all active catalyst is deactivated; (2) purifying the monomer or comonomer by directing the monomer or comonomer through the at least one purification unit before entry into the at least one reactor; or (3) providing critically clean catalyst feed vessels. In preferred embodiments, all of the three steps or acts are employed.

25   The term "interpolymer" is used herein to indicate a copolymer, a terpolymer, a tetrapolymer, etc. That is, at least one other comonomer is polymerized with ethylene or other olefins to make an interpolymer. Suitable ethylene interpolymers which are produced from the reactor system comprise ethylene with at least one C_3-C_{20} α-olefin and/or C_4-C_{18} diolefin. Preferred comonomers include the one C_3-C_{20} α-olefins, especially propylene,

30   isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, and 1-

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decene, more preferably 1-butene, 1-hexene, heptene and 1-octene. Most preferably, the ethylene interpolymer is a copolymer of ethylene and 1-butene.

In a preferred embodiment, the process system, as shown in Fig. 1, comprises a reactor R1, a catalyst feed vessel V1, a first post reactor vessel V2, and a second post reactor vessel V3. A first monomer (S1), preferably ethylene, a chain terminating agent (S2), preferably hydrogen, and a solvent (S3), preferably butene, are fed to the reactor R1. The reactor R1 and the first post reactor vessel V2 are preferably jacketed and equipped with a means for agitation. The catalyst feed vessel V1 is also equipped with a means for agitation. The temperature of the reactor R1 ranges from about is from 20 to 115 °C, preferably from 50 to 105 °C. However, the upper limit of the polymerization temperature is a temperature which is highest among temperatures at which the ethylene copolymer produced can maintain substantially a powdery state. This temperature varies depending on the density of the ethylene copolymer produced and the type of diluent used. The pressure of the reactor R1 ranges from about 1 to about 100 atm, preferably from about 3 to about 30 atm. Catalyst (S4) from the catalyst feed vessel V1 is also fed to the reactor R1.

The molar ratio of catalyst/cocatalyst employed preferably ranges from 1:10,000 to 100:1, more preferably from 1:5000 to 10:1, most preferably from 1:1000 to 1:1. Alumoxane, when used by itself as an activating cocatalyst, is generally employed in large quantity, generally at least 100 times the quantity of metal complex on a molar basis. The remaining activating cocatalysts are generally employed in approximately equimolar quantity with the metal complex.

In general, the polymerization may be accomplished at conditions known in the art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from -50 to 250 °C, preferably 30 to 200 °C and pressures from atmospheric to 10,000 atmospheres. Suspension, solution, slurry, gas phase, solid state powder polymerization or other process condition may be employed if desired. A support, especially silica, alumina, or a polymer (especially polytetrafluoroethylene or a polyolefin) may be employed, and desirably is employed when the catalysts are used in a gas phase or slurry polymerization process. Preferably, the support is passivated before the addition of the catalyst. Passivation techniques are known in the art, and include treatment of the support with a passivating agent such as triethylaluminum. The support is preferably employed in an amount to provide a

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weight ratio of catalyst (based on metal):support from about 1:100,000 to about 1:10, more

preferably from about 1:50,000 to about 1:20, and most preferably from about 1:10,000 to

about 1:30. In most polymerization reactions, the molar ratio of catalyst:polymerizable

compounds employed preferably is from about $10^{-12}:1$ to about $10^{-1}:1$, more preferably from

5   about $10^{-9}:1$ to about $10^{-5}:1$.

Suitable solvents for polymerization are inert liquids. Examples include, but are not

limited to, straight and branched-chain hydrocarbons such as isobutane, butane, pentane,

hexane, heptane, octane, and mixtures thereof; mixed aliphatic hydrocarbon solvents such as

kerosene and ISOPAR (available from Exxon Chemicals), cyclic and alicyclic hydrocarbons

10   such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures

thereof; perfluorinated hydrocarbons such as perfluorinated C_{4-10} alkanes, and the like, and

aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene,

ethylbenzene and the like. Suitable solvents also include, but are not limited to, liquid olefins

which may act as monomers or comonomers including ethylene, propylene, butadiene,

15   cyclopentene, 1-hexene, 1-hexane, 4-vinylcyclohexene, vinylcyclohexane, 3-methyl-1-

pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene, styrene, divinylbenzene,

allylbenzene, vinyltoluene (including all isomers alone or in admixture), and the like.

Mixtures of the foregoing are also suitable.

The catalysts may be utilized in combination with at least one additional

20   homogeneous or heterogeneous polymerization catalyst in separate reactors connected in

series or in parallel to prepare polymer blends having desirable properties. An example of

such a process is disclosed in WO 94/00500, equivalent to U. S. Serial Number 07/904,770,

as well as U. S. Serial Number 08/10958, filed January 29, 1993. The disclosures of the

patent applications are incorporated by references herein in their entirety.

25   The catalyst system may be prepared as a homogeneous catalyst by addition of the

requisite components to a solvent in which polymerization will be carried out by solution

polymerization procedures. The catalyst system may also be prepared and employed as a

heterogeneous catalyst by adsorbing the requisite components on a catalyst support material

such as silica gel, alumina or other suitable inorganic support material. When prepared in

30   heterogeneous or supported form, it is preferred to use silica as the support material. The

heterogeneous form of the catalyst system may be employed in a slurry polymerization. As a

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practical limitation, slurry polymerization takes place in liquid diluents in which the polymer product is substantially insoluble. Preferably, the diluent for slurry polymerization is one or more hydrocarbons with less than 5 carbon atoms. If desired, saturated hydrocarbons such as ethane, propane or butane may be used in whole or part as the diluent. Likewise the α-olefin

5   monomer or a mixture of different α-olefin monomers may be used in whole or part as the diluent. Most preferably, the major part of the diluent comprises at least the α-olefin monomer or monomers to be polymerized.

Solution polymerization conditions utilize a solvent for the respective components of the reaction. Preferred solvents include, but are not limited to, mineral oils and the various

10   hydrocarbons which are liquid at reaction temperatures and pressures. Illustrative examples of useful solvents include, but are not limited to, alkanes such as pentane, iso-pentane, hexane, heptane, octane and nonane, as well as mixtures of alkanes including kerosene and Isopar E™, available from Exxon Chemicals Inc.; cycloalkanes such as cyclopentane, cyclohexane, and methylcyclohexane; and aromatics such as benzene, toluene, xylenes,

15   ethylbenzene and diethylbenzene.

At all times, the individual ingredients, as well as the catalyst components, should be protected from oxygen and moisture. Therefore, the catalyst components and catalysts should be prepared and recovered in an oxygen and moisture free atmosphere. Preferably, therefore, the reactions are performed in the presence of a dry, inert gas such as, for example,

20   nitrogen or argon.

The polymerization may be carried out as a batch or a continuous polymerization process. A continuous process is preferred, in which event catalysts, solvent or diluent (if employed), and comonomers (or monomer) are continuously supplied to the reaction zone and polymer product continuously removed therefrom. The polymerization conditions for

25   manufacturing the interpolymers according to embodiments of the invention are generally those useful in the solution polymerization process, although the application is not limited thereto. Gas phase and slurry polymerization processes are also believed to be useful, provided the proper catalysts and polymerization conditions are employed.

In some embodiments, the polymerization is conducted in a continuous solution

30   polymerization system comprising two reactors connected in series or parallel. One or both reactors contain at least two catalysts which have a substantially similar comonomer

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incorporation capability but different molecular weight capability. In one reactor, a relatively high molecular weight product (M_w from 100,000 to over 1,000,000, more preferably 200,000 to 1,000,000) is formed while in the second reactor a product of a relatively low molecular weight (M_w 2,000 to 300,000) is formed. The final product is a mixture of the two

5   reactor effluents which are combined prior to devolatilization to result in a uniform mixing of the two polymer products. Such a dual reactor/dual catalyst process allows for the preparation of products with tailored properties. In one embodiment, the reactors are connected in series, that is the effluent from the first reactor is charged to the second reactor and fresh monomer, solvent and hydrogen is added to the second reactor. Reactor conditions

10   are adjusted such that the weight ratio of polymer produced in the first reactor to that produced in the second reactor is from 20:80 to 80:20. In addition, the temperature of the second reactor is controlled to produce the lower molecular weight product. In one embodiment, the second reactor in a series polymerization process contains a heterogeneous Ziegler-Natta catalyst or chrome catalyst known in the art. Examples of Ziegler-Natta

15   catalysts include, but are not limited to, titanium-based catalysts supported on $MgCl_2$, and additionally comprise compounds of aluminum containing at least one aluminum-alkyl bond. Suitable Ziegler-Natta catalysts and their preparation include, but are not limited to, those disclosed in US Patent 4,612,300, US 4,330,646, and US 5,869,575. The disclosures of each of these three patents are herein incorporated by reference.

20   Suitable catalysts include, but are not limited to, metallocene or single-site catalyst systems. Preferably, the single-site or metallocene catalyst is a constrained geometry catalyst system as described in WO 96/16092, WO 98/27119, and WO 96/28480, the disclosures of which are incorporated herein by reference. More preferably, the metallocene or single-site catalyst is supported using an inert material such as, for example, silica. More preferably, the

25   single-site or metallocene catalyst is reacted with a suitable co-catalyst (e.g., a boron-containing compound or an alumoxane) which is bonded or fixed to the support in a prior step such that the single-site or metallocene catalyst is immobilized to the extent that substantially no soluble catalyst species is extracted from the support during polymerization, most preferably the species are fixed or bonded such that there is substantially no extraction

30   when the solid catalyst system is boiled in toluene for 2 hours. Suitable single-site catalyst systems for use in manufacturing the novel composition are also described in detail in US

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Patent Nos. 6,043,180 and 5,834,393, the disclosures of which are incorporated herein by reference. The supported catalyst systems used in polymerization make interpolymers with reverse comonomer distribution ("RCD"). The characteristics of these interpolymers, including RCD, are described in U.S. Provisional Application Serial No. 60/313,357, filed on

5 August 17, 2001, entitled "BIMODAL POLYETHYLENE COMPOSITION AND ARTICLE MADE THEREFROM," in names of Jozef J. Van Dun *et al.*, the disclosure of which is incorporated herein by reference.

During production, polymer (S5) is transferred to either the first post reactor vessel V2 or the second post reactor vessel V3. If polymer (S5) is transferred to the second post

10 reactor vessel V3, the unreacted monomers and diluent are removed. In an optional embodiment, conditions exist where the active catalyst can continue polymerizing under very low hydrogen ethylene ratio conditions. For the catalysts described above, hydrogen concentration drops faster than ethylene concentration due to the catalyst's intrinsic high consumption rate of hydrogen vs ethylene, and/or due to venting of the vessel since hydrogen

15 is preferentially vented vs ethylene due to the fact that hydrogen has a lower solubility. The post reactor vessels are not part of the reactor. They are separate from the reactor and have their own operating temperatures and pressures. The operating conditions of the post reactor vessels may be similar to the reactor or they may be different.

If polymer (S5) is transferred to the first post-reactor vessel V2, the terminator (S2)

20 concentration is relatively important in metallocene or single-site catalyst systems. It has been found that some of these catalysts have exceptionally high terminator reactivity/consumption rates relative to Ziegler-Natta or chromium catalysts. Accordingly, in preferred embodiments, the concentration for chain terminator agents in the post-reactor environment is kept in the range of about 0.001 to about 0.5 mole of terminator per mole of

25 ethylene. Below 0.001 mole terminator to mole ethylene, undesirable gel formation occurs and above 0.5 mole terminator to mole ethylene, undesirable oligomer formation occurs. More preferably, the range of from about 0.01 to about 0.4 or about 0.05 to about 0.2 mole of terminator to mole ethylene is maintained.

Chain terminators are also know as chain transfer agents or telogens which are used to

30 control the melt flow index in a polymerization process. Chain transfer involves the termination of growing polymer chains, thus limiting the ultimate molecular weight of the

polymer material. Chain transfer agents are typically hydrogen atom donors that will react with a growing polymer chain and stop the polymerization reaction of said chain. These agents can be of many different types, from saturated hydrocarbons or unsaturated hydrocarbons to aldehydes, ketones or alcohols. By controlling the concentration of the

5 selected chain transfer agent, one can control the length of polymer chains, and, hence, the weight average molecular weight, M_w The melt flow index (MFI or I_2) of a polymer, which is related to M_w, is controlled in the same way.

After the donation of a hydrogen atom, the chain transfer agent forms a radical which can react with the monomers, or with already formed oligomers or polymers, to start a new

10 polymer chain. This means that any functional groups present in chain transfer agents, for instance, carbonyl groups of aldehydes and ketones, will be introduced in the polymer chains.

Any chain terminator agents known or presently unknown in the art may be used in embodiments of the invention. But preferred chain terminator agents include hydrogen, propylene and isobutane, with hydrogen being most preferred. The term "chain terminator

15 agent" is used interchangeably in the art with the terms "chain transfer agent" and "telogen".

A large number of chain transfer agents, for example propylene and 1-butene which have an olefinically unsaturated bond, can also be incorporated in the polymer chain, themselves, via a copolymerization reaction. This generally leads to the formation of short chain branching of respectively methyl and ethyl groups, which lowers the density of the

20 polymers obtained.

Another process for reducing the amount of HMW gels in the polymer product, is by using a critically clean catalyst feed vessel. By the term "critically clean catalyst feed vessel", it is meant that only disposable or one-time-use catalyst vessels are used or, when reusable catalyst vessels are used, prior to use they are cleaned by the following exemplary

25 procedure: as in ordinary cleaning, the contents of the catalyst vessel are drained and the vessel is rinsed with hexane or other diluents or solvents until it is visually free of solids. The catalyst vessel is then dried with N_2. In some embodiments, the catalyst vessel is filled with a mixture of hexane and isopropanol (concentration: 1:1 hexane/alcohol molar ratio) to a liquid level at least as high as the level of the previously contained catalyst system. The

30 alcohol/hexane mixture is then agitated for 2-3 hours and afterwards drained. The drained/empty vessel is then flushed with N_2 for 1 hour and then rinsed with hexane. The

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vessel is then filled with hexane and stirred for 1 hour and then drained and purged with N_2 for 1 hour. The hexane rinsing steps of stirring for 1 hour and purging with N_2 for 1 hour (or until dry) is then repeated. It should be understood that variations from the above procedure are acceptable so long as substantially similar results are achieved.

5   The critical cleaning procedure involves cleanup of the catalyst holding and feed vessels and catalyst feed lines to the reactors. It is effective in removing Ziegler-Natta catalyst or chromium catalyst residues and contaminants, and making the catalyst storage and feed lines and pumps suitable for use with a metallocene or single-site catalyst system. The process described herein is suitable for use in manufacturing olefin homopolymers or

10   interpolymers, especially ethylene homopolymers as well as ethylene interpolymers.

The cleaning method described above may be used during startup or when transitioning between different and/or incompatible catalysts. The catalysts are incompatible due to different reactivity ratios for molecular weight regulators and comonomers. They may detrimentally react with each other and reduce the activity of one or both catalysts. The

15   method may be used in gas phase, solution phase or slurry phase polymerization process systems. It may also be used in a two stage reactor system having two different catalysts.

Impurities in ethylene and possibly in the solvent feedstream can cause reactor fouling when using metallocene or single site catalysts. In-situ ethylene purification is preferably accomplished with the use of molecular sieve and/or activated alumina beds. As

20   shown in Fig. 2A, ethylene (Q3) from a pipeline is fed to a first purification unit P1. Alternatively, a second purification unit P2 may be in series or parallel with the first purification unit P1. The purification units, P1 and P2 may be bypassed by a series of valves (all of which are not shown). This gives the operator flexibility on the degree of purity (Q2 or Q3) to be sent to the reactor R1. The first purification unit P1 and the second purification

25   unit P2 are preferably filled with a molecular sieve or activated alumina bed for removing impurities from the ethylene. The molecular sieve may be of the zeolite type. The activated alumina may be of the gel, psuedoboehmite, gamma or bayerite type aluminas . In a preferred embodiment of the invention, in addition to in-situ purification of ethylene, process diluent and solvent as well as comonomer fed streams are also in-situ purified.

30   Process steps described above can be practiced in a gas phase, solution phase or slurry phase polymerization process system but they are particularly suitable for use in gas phase

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and slurry polymerization. These process steps can be used for a single-reactor polymerization system or a multiple reactor polymerization system either configured in series or in parallel. They can also be used in a multiple reactor system where there is separate fresh catalyst injection in each reactor as well as where there is fresh catalyst injection in the

5   first reactor only.

In a multiple reactor polymerization system, post-reactor equipment and vessels exist after each reactor and intermediate to the next subsequent reactor. Thus, in a two reactor system, there are two post-reactor environment where the ratio of terminator to ethylene should be specifically controlled to provide a high level of terminator to avoid gel and

10   extraneous HMW polymer fraction formation. Other suitable reactor systems are disclosed, for example, in WO 95/26370, WO 96/39450 and WO 97/32905, the disclosures of which are incorporated herein by reference in their entirety. The disclosed reactor systems may be used in embodiments of the invention with or without modifications.

By the term "extraneous high molecular weight polymer fraction" as used herein, it is

15   meant that the HMW polymer fraction that is or was formed was not purposefully intended; that is, the fraction exists as an artifact of the intended bulk polymer. More particularly, the extraneous fraction was not formed in the reactor, it was formed in a post-reactor environment.

By the term "low gels" or "low extraneous HMW polymer fraction", as used herein, it

20   is meant that the visual gel count on a 10 cm x 10 cm x 25 mm film fabricated at a melt temperature in the range of about 200 to about 212 °C will be less than about 300 gels/gram of film, preferably, less than or equal to about 250 gels/gram of film, more preferably, less than or equal to about 100 gels/gram of film and, most preferably, less than or equal to about 75 gels/gram of film.

25   The following examples are presented to illustrate various embodiments of the invention. They are not intended to be representative of all embodiments of the invention and should be not construed to limit the scope of the claimed invention as described here. All numbers described herein are approximate values and may vary within their accuracy ranges.

In the following illustrative examples, density was measured in accordance with

30   ASTM D-792. Melt index measurements were performed according to ASTM D-1238, Condition 190°C/2.16 kilogram (kg) and Condition 190 °C/5 kg, and are known as I_2 and I_5,

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respectively. Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. Melt index is reported as g/10 minutes.

EXAMPLES

5   Experiment 1

An experiment was conducted to determine the effect of terminator concentration in post-reactor environment on the gel level of corresponding products. For this experiment, a supported constrained geometry catalyst system was prepared following methods disclosed in WO 98/27119, Example 12. In a small, pilot polyethylene slurry polymerization facility, two
10   (2) sample taking points were devised as shown in FIG. 1: first post reactor vessel V2 and second post reactor vessel V3.

The first post reactor vessel V2 was operated at a low pressure (0.2 barg) at 70°C, and was continuously purged with N_2 and vented. In this way, the polymer slurry entering the first post reactor vessel V2 was dried. Because of the low pressure, N_2 purging and venting,
15   polymerization could not occur in the first post reactor vessel V2.

The second post reactor vessel V3 was designed to collect a slurry polymer sample directly from the reactor. The second post reactor vessel V3 had no insulation or cooling and thus the temperature at the device was lower than the reactor temperature. The pressure at the start of the experiment was about 2 to about 4 barg. During sampling, no venting took
20   place and the pressure increased to about 6 to about 7 bar. After sampling, the solvent was filtered from the polymer with N_2 pressure. After this step, the second post reactor vessel V3 was purged with N_2, then depressurized to atmospheric pressure. At these conditions, polymerization could continue. Second post reactor vessel V3 was then opened and the powder was collected in a drum wherein unreacted ethylene and hydrogen were permitted to
25   vent.

The samples were alternatively taken from the first post reactor vessel V2 (inventive example 1) and from the second post reactor vessel V3 (comparative run 1) during lined-out reactor conditions. During the sampling procedure, reactor was switched back and forth (about every 30 minutes) between the first post reactor vessel V2 and the second post reactor
30   vessel V3. In this way, sufficient and representative resins were sampled under exactly identical reactor conditions.

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All samples were produced under the same reactor conditions for homopolymer production: Reactor temperature = 70°C, Reactor pressure = 12 barg, hexane flow = 2800 g/hr. Additional process details are provide in Table 1 below.

TABLE 1

	Ethylene flow rate [g/h]	Hydrogen flow rate [Nl/h]	Vent flow rate [g/h]	Catalyst Yield [gPe/gTi]
Inv. Example 1A	823	0.8085	44.761	531,000
comparative run 1A	824	0.8084	44.917	531,000
Inv. Example 1B	834	0.856	45.28	669,000
comparative run 1B	884	0.9145	45.08	642,000

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The gel quality of resultant samples was measured by blowing film samples on a Haake film extruder (4.2 m long, thickness between 0.055 and 0.065 mm, layflat 75 mm, i.e. 10,000 in^2) at a melt temperature of about 210°C. The total visual gel count on a 10 by 10 cm film sample was then converted into gels/g and are reported below in Table 2.

10   TABLE 2

	Sampling point	I_2 (g/10 min)	Density (g/cm^3)	Gel count gels/gr
Inv. Example 1A	9	1.02	0.9610	179
Comparative run 1A	12	1.07	0.9615	499
Inv. Example 1B	9	0.86	0.9601	45
Comparative run 1B	12	0.73	0.9609	1,279

As shown in Table 2, the gel count of the inventive examples were substantially lower than the gel count for the comparative examples. As such, this experiment demonstrated that, under above conditions for the second post reactor vessel V3, unreacted ethylene and hydrogen (the chain terminator agent) continued to react in a batch-wise mode wherein hydrogen was consumed much faster than the ethylene resulting in an imbalance which led to the formation of high molecular weight polymer and ultimately gels. Alternatively, by maintaining a high hydrogen level at the first post reactor vessel V2, substantially reduced levels of gels were obtained.

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Experiment 2

Another experiment was conducted to determine the effect of purification of the ethylene feed stream on the resistance to the onset of reactor fouling and sheeting. The

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polymerization system (FIG. 1) used in this experiment consisted of a single reactor R1 having a volume of 10 liter (no baffles) and equipped with a Lightnin A310 mixing blade running at about 750 rpm. All feed streams were fed through dip pipe legs in the liquid phase to allow intimate mixing. The reactor was operated at about 70 °C and a constant pressure of

5   about 12 bar. The reactor temperature was kept constant by jacket cooling and the pressure was kept constant by controlling the ethylene feed rate. The catalyst was pulsed into the main hexane diluent stream. The reactor level was kept at about 75 % of the total volume by discontinuously dumping the reactor content to the flash vessel. In this flash vessel (operating at a pressure of about 1.3 bar and a temperature of about 75 °C), the diluent and

10   unreacted monomers are evaporated and vented, resulting in a dry powder. The reactor was vented continuously to allow for gas analysis using an on-line gas chromatograph (GC). The GC provided an analysis of the reactor head space about every 6 minutes. The production rate was controlled by the catalyst flow and was calculated based on ethylene feed flow minus the vent flow through the vent. The diluent used was hexane.

15   The I_2 melt index of the polymer for the runs was controlled via hydrogen addition to the reactor, the density was controlled via comonomer addition to the reactor, and in all cases the comonomer was 1-butene, if present. Based on the polymer production and catalyst consumption, the catalyst efficiency was also calculated.

            The catalyst used in this experiment was a supported borate constrained geometry

20   catalyst system prepared as follows: Silica gel (948 grade available from Grace-Davidson) was dehydrated at an elevated temperature to a total volatiles of ca. about 3 wt. %. 24.71 kg of the resulting silica was slurried in 130 liters of dry hexane and then treated with 30.88 kg of a 1.21 M solution of triethylaluminum (TEA) in hexane. The slurry was filtered and washed with fresh, dry hexane (130 liters per wash) at ambient until the residual aluminum in

25   the wash was < 0.5 mmol/L. The solids were then isolated by filtration and dried under vacuum (~ 10 torr) at about 60 °C to a residual solvent level of less than or equal to about 1.0 wt. %. 1.5 moles of $[NHMe(C_{18-22}H_{37-45})_2]$ $[HOC_6H_4B(C_6F_5)_3]$, as 16.95 kg of a 10.1 wt. % solution in toluene, was diluted by addition of 9.61 liters (8.32 kg) toluene. This solution was allowed to agitate for about 10 minutes and then about 1.65 moles of TEA, as 0.88 liters

30   (0.76 kg), of a 1.87 M solution of TEA in toluene was added and the resulting solution allowed to mix for 15 minutes. Then the solid silica/TEA was added over approximately 30

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minutes. On completion of the addition, the impregnated material was allowed to mix for about 60 minutes. With continuous agitation, about 195 liters (128.7 kg) of dry, fresh hexane at ambient was added to the solid and the resulting slurry was allowed to agitate for about 30 minutes. Then 1.2 moles of a constrained geometry catalyst, $(C_5Me_4SiMe_2N^tBu)Ti(\eta^4-1,3-$

5   pentadiene) (as 3.69 kg of a 0.223 M solution in heptane), was added and the slurry was mixed for about 2 hours. The solvent was removed from the slurry by filtration and the resulting solid washed four times with dry, fresh hexane at ambient and dried under vacuum to provide a free flowing powder.

In this experiment, single reactor runs were conducted at three (3) different ethylene

10   impurity levels to produce copolymer samples having a melt index I_2 of about 1.5 g/10 min and a density of about 0.940 g/cm^3. The first run was initiated with a pristine clean reactor and catalyst feed line. After each run, the reactor was disassembled, photographed and stripped clean to a pristine condition for the subsequent run.

The ethylene at different impurity levels was obtained by different levels of

15   purification. That is, ethylene purity as received from the pipeline contained the highest concentration of impurities and was designated Q3. Q3 ethylene was purified using an adsorption bed (P1) filled with 50% mol-sieve 3A and 50% Selexsorb™ COS material. With purification unit P1 in service, the ethylene quality was improved from level Q3 (before the purification unit P1) to quality Q2 (after the purification unit P1). Also, a second purification

20   unit (P2) was used in series with the P1 unit. Unit P2 consisted of a smaller size purification bed, filled with mol-sieve 3A. Ethylene passed through P1 and P2 was designated Q1 quality ethylene. FIG. 2A shows scheme for ethylene purification. The process conditions including total run time, GC gas analysis and product properties are shown in Table 3 for the various runs.

25   Table 3 indicates that when ethylene purity increases (i.e. improves), the run time increased. Also, catalyst productivity/efficiency substantially increased with increasing ethylene purity, and less fine particles were produced. But also, less lumps (defined as powder particles > 2 mm) were produced with increasing purity level. Table 4 provides the visual assessment of the various runs and FIGS. 3A - 3D show photos of the reactor taken

30   just after the various runs. These results illustrate that substantial reductions in the onset of reactor fouling and sheeting result with increased ethylene purity. In particular, Table 3

Experiment 4

In still another series of tests, ethylene with different impurity concentrations obtained by different levels of purification is used to produce polyethylene in a slurry miniplant. Single reactor experiments were conducted to produce a homopolymer polyethylene with a

5 melt index I_2 = 150 g/10 min from different purity levels of an ethylene feed stream. The purification unit P1 was replaced (swapped) during operation at varying time intervals. The purification system is similar to the one described in Fig. 2A and is illustrated in Fig. 2B.

Ethylene used comes from the pipeline (pipeline quality). In the following examples, this ethylene is called Q3 quality ethylene and contains the highest concentration of

10 impurities. The ethylene can be purified by using an adsorption bed (P2) filled with either Molesieve 3A (from UOP), Selexsorb CD (activated alumina from Alcoa) or Selexsorb COS (activated alumina from Alcoa). When this purification unit (P2) is put into service, the ethylene quality is improved from level Q3 (Before the purification unit P2) to quality Q4A (when P2 is filled with Molesieve 3A), Q4B (when P2 is filled with Selexsorb CD) or Q4C

15 (when P2 is filled with Selexsorb COS) after the purification unit P2. A second purification unit (P3) can be used, in series with the P2 unit filled. Unit P3 consists of a same size purification bed as P2, filled with Selexsorb CD or Selexsorb COS. In this way, the purity of ethylene with quality Q4A can be improved to quality Q5A (with molesieve 3A in P2 and Selexsorb CD in P3) or to quality Q5B (with molesieve 3A in P2 and Selexsorb COS in P3).

20 Also the ethylene with quality Q4B can be improved to quality Q5C (with Selexsorb CD in P2 and Selexsorb COS in P3).

The catalyst used was a solid supported borate CGC catalyst as described above for Example 2. The experiments were continued until stable operation was no longer possible.

TABLE 6

Experiment			4A	4B	5	6
Ethylene Purity			Q1	Q1	Q2	Q1B
Reactor conditions	Reactor pressure	barg	12	12	12	12
	Reactor temperature	°C	70	70	70	70
	Catalyst flow	g cat/h	1.512	1.92		
	Hexane flow	g/h	3500	3500	3500	3500
	Hydrogen flow	Nl/h	7.735	7.81	5.7	9.5
	Ethylene flow	g/h	1682	1669	1713	1670
	Reactor vent flow	Nl/h	45	45	45	45
	Production rate	g PE/h	1474	1476	1500	1450
Total run time		Hrs	12.5	11	4.75	25.5

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Catalyst Productivity		Kg PE/ g Ti	510	396	-	450
Reactor head space	Nitrogen	Vol %	2.87	2.76	3.92	2.24
	Hydrogen	Vol %	1.09	1.09	1.05	1.26
	Ethylene	Vol %	88.49	87.7	86.6	92.2
	Ethane	Vol %	0.29	0.30	0.34	0.65
	Hexane	Vol %	2.89	3.01	2.82	3.24
Powder properties	Melt index I2	g/10 min	137	128	-	-
	Bulk Density	g/ cm^3	0.434	0.433	-	-
	Powder D50	μm	551	544	-	-

When the ethylene purification is improved by repeatedly switching the purification bed, the run time is drastically increased. The U'-value was monitored during the runs. The U'-value is the heat transfer coefficient across the reactor wall and is defined by the heat

5   transferred through the reactor wall divided by the temperature difference over the reactor wall and is expressed in units [kJ/K/hr]. The U'-value is a measure of the fouling on the wall of the reactor.

Figure 4 shows the U'-value of the reactor wall during the 4 experiments. The vertical lines show the times at which the P1 purification units have been swapped in experiment 6.

10   The U'-value plots in this graph clearly show that the fouling rate is lower with better purification.

Example 5

In another series of tests, ethylene treated with different purification adsorbents is used to produce polyethylene in a slurry miniplant. Single reactor experiments were

15   conducted to produce a homopolymer polyethylene with a melt index I_2 = 150 g/10 min. Experiments with different ethylene purification adsorbents were performed to determine the influence of ethylene purification adsorbents on the reactor fouling performance.

As shown in Fig. 2B, ethylene is used that comes from the pipeline (pipeline quality). In this example, this is called Q3 quality ethylene and contains the highest concentration of

20   impurities. The ethylene can be purified by using an adsorption bed (P1) filled with either Molesieve 3A (from UOP), Selexsorb CD (activated alumina from Alcoa) or Selexsorb COS (activated alumina from Alcoa). When this purification unit (P1) is put into service, the ethylene quality is improved from level Q3 (Before the purification unit P1) to quality Q4A (when P1 is filled with Molesieve 3A), Q4B (when P1 is filled with Selexsorb CD) or Q4C

25   (when P1 is filled with Selexsorb COS) after the purification unit P1.

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A second purification unit (P2) can be used, in series with the P1 unit filled. Unit P2 consists of a same size purification bed as P1, filled with Selexsorb CD or Selexsorb COS. In this way, the purity of ethylene with quality Q4A can be improved to quality Q5A (with molesieve 3A in P1 and Selexsorb CD in P2) or to quality Q5B (with molesieve 3A in P1 and Selexsorb COS in P2). Also the ethylene with quality Q4B can be improved to quality Q5C (with Selexsorb CD in P1 and Selexsorb COS in P2).

In all these experiments freshly regenerated beds were used at the beginning of each experiment. Purification beds were not swapped during an experiment. The catalyst used was a solid supported borate CGC catalyst as described above for Example 2.

The experiments 7 (Q4A), 10 (Q5A) and 11 (Q5B) have run until yield and U'value have dropped to 70% of the original value or unless it was impossible to run the reactor without large temperature deviations from the reactor temperature setpoint. Experiments 8 (Q4B) and 9 (Q4C) have only been allowed to run for 19 hr before shutdown. Experiment 12 (Q5C) was shutdown after 57 hr due to operational issues that were not caused by reactor operation. This run had prematurely failed.

TABLE 7

Experiment			7	8	9	10	11	12
Ethylene Purity			Q4A	Q4B	Q4C	Q5A	Q5B	Q5C
Reactor conditions	Reactor pressure	barg	12	12	12	12	12	12
	Reactor temperature	°C	70	70	70	70	70	70
	Catalyst flow	g cat/h	1.74	1.44	1.38	1.5	1.404	1.512
	Hexane flow	g/h	3500	3500	3500	3500	3500	3500
	Hydrogen flow	Nl/h	8.36	8.7	8.26	8.3	8.1	7.8
	Ethylene flow	g/h	1688	1754	1723	1724	1681	1762
	Reactor vent flow	g/h	150	150	150	150	150	150
	Production rate	g PE/h	1465	1530	1500	1501	1458	1536
Total run time		Hrs	22	19	19	72	72	57
Catalyst Productivity		Kg PE/ g Ti	445	550	575	533	534	530
Reactor head space	Nitrogen	Vol %	2.03	1.49	1.47	1.66	2.07	1.41
	Hydrogen	Vol %	1.11	1.1	1.11	1.09	1.09	1.02
	Ethylene	Vol %	93.01	93.21	93.95	93.65	93.68	92.55
	Ethane	Vol %	0.48	0.36	0.35	0.4	0.4	0.32
	Hexane	Vol %	3.04	3.19	3.37	3.26	3.36	3.95
Powder properties	Melt index I2	g/10 min	144	167	141	153	150	146
	Bulk Density	g/ cm^3	0.403	0.43	0.44	0.385	0.391	0.384
	Powder D50	µm	523	550	553	540	532	553

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When the ethylene purification is improved by using multiple and different purification beds, the run time is drastically increased. The U'-value was monitored during the runs. The U'-value is the heat transfer coefficient across the reactor wall and is defined by the heat transferred through the reactor wall divided by the temperature difference over the reactor wall and is expressed in units [kJ/K/hr]. The U'-value is a measure of the fouling on the wall of the reactor. Fig. 5 shows the U'-value of the reactor wall during the above described experiments.

As demonstrated above, embodiments of the invention provide a polymerization process and system which produces polymers with less gels or extraneous high molecular weight polymer fractions. The reactor system, when operated in accordance with embodiments of the invention, exhibits a reduced level of reactor fouling and/or sheeting. As a result, the runtime and thus the efficiency of the reactor system has increased. Other advantages are apparent to those skilled in the art.

While the invention has been described with respect to a limited number of embodiments, the specific features of one embodiment should not be attributed to other embodiments of the invention. No single embodiment is representative of all aspects of the inventions. Moreover, variations and modifications therefrom exist. For example, while the production of ethylene interpolymers is preferred use of the processes described herein, the processes can be applied to manufacture any polymer. The processes are described in terms of one or more steps or acts, it should be understood that the process can be practiced in any order or sequence of the acts or steps. Although particle-form polymerization is the preferred use of the processes, they may also be employed for non-particle-form polymerization, such as continuous solution polymerization, with or without modifications. Finally, equivalent catalysts to metallocene or constrained geometry catalysts may be used instead. The appended claims intend to cover all such variations and modifications as falling within the scope of the invention.

What is claimed is:

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1   1.   A polymerization process for making a polymer, the polymer comprising ethylene and
2   characterized as having low levels of gels, and the process comprising:
3   (I)   providing a polymerization system comprising:
4   (a)   at least one by-passable purification unit,
5   (b)   at least one catalyst feed vessel,
6   (c)   at least one reactor, and
7   (d)   post-reactor equipment and vessels which are separate from the at least
8   one reactor, and
9   (II)   continuously polymerizing ethylene and optional comonomers in the at least
10   one reactor in the presence of an active catalyst which is continuously fed to the reactor,
11   continuously transferring the polymerized ethylene and the optional comonomers from the
12   reactor to the post-reactor equipment and vessels and:
13   (a)   providing a chain terminator in the post-reactor equipment and vessels
14   and maintaining a molar ratio of chain terminator to ethylene of from
15   about 0.001 to about 0.5 in the post-reactor until all active catalyst is
16   deactivated, or
17   (b)   purifying the ethylene by directing the ethylene through the at least
18   one purification unit before entry into the at least one reactor, or
19   (c)   providing critically clean catalyst feed vessels, or
20   (d)   any combination of (a)-(c).

1   2.   The process of Claim 1 wherein the ethylene polymer is characterized as
2   having a visual gel count of less than or equal to 250 gels per gram of film.

1   3.   The process of Claim 1 wherein the polymerization system comprising at least
2   two ethylene purification units.

1   4.   The process of Claim 3 wherein the two ethylene purification units comprise
2   molecular sieve beds.

1   5.   The process of Claim 1 wherein the process is characterized as providing a

2   runtime of greater than or equal to 15 hours per 600 pounds of produced polymer/hour per 10

3   liters of reactor volume before the onset of reactor fouling and sheeting.

1   6.   The process of Claim 1 wherein the critically clean catalyst vessel is provided

2   by the use of a disposable or single-use catalysts vessel.

1   7.   The process of Claim 1 wherein the critically clean catalyst vessel is provided

2   by using the cleaning procedure comprising a polar compound.

1   8.   The process of Claim 7 wherein the polar compound is selected from alcohol

2   or water.

1   9.   The process of Claim 1 wherein the chain terminator agent is hydrogen.

1   10.   The process of Claim 1 wherein the chain terminator agent is maintained in

2   the post reactor system at a level in the range of from about 0.01 to about 0.4 mole of

3   terminator to mole ethylene.

1   . 11.   The ethylene polymer obtainable by the process of Claim 1.

1   12.   The ethylene polymer of Claim 11 wherein the polymer is an interpolymer.

1   13.   The ethylene polymer of Claim 11 wherein the polymer is manufactured using

2   a supported metallocene catalyst system.

1   14.   The ethylene polymer of Claim 13 wherein the metallocene catalyst system is
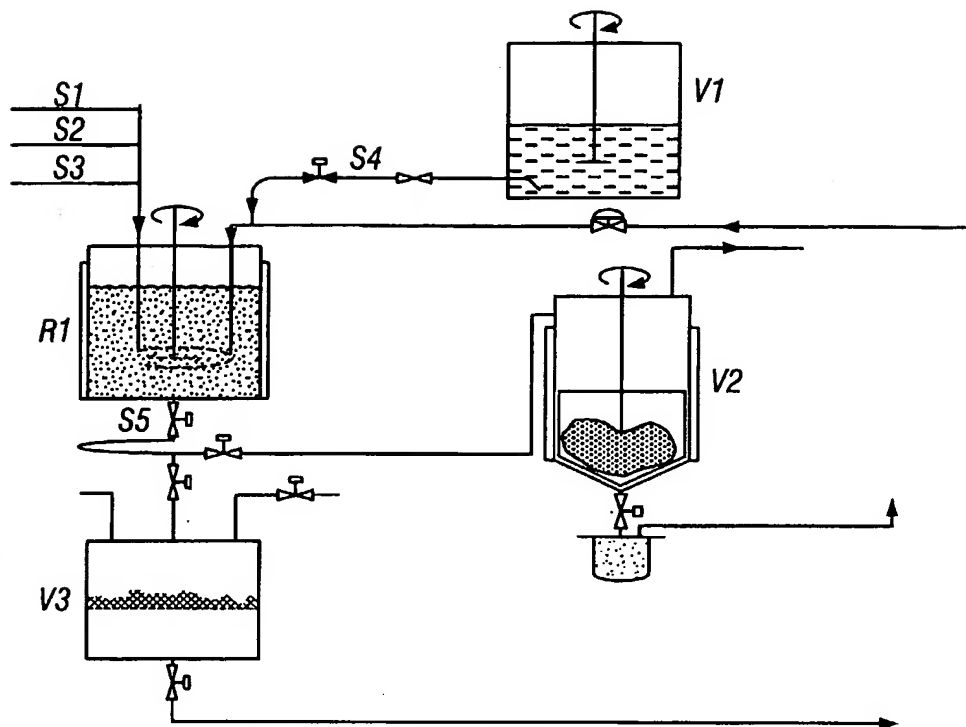
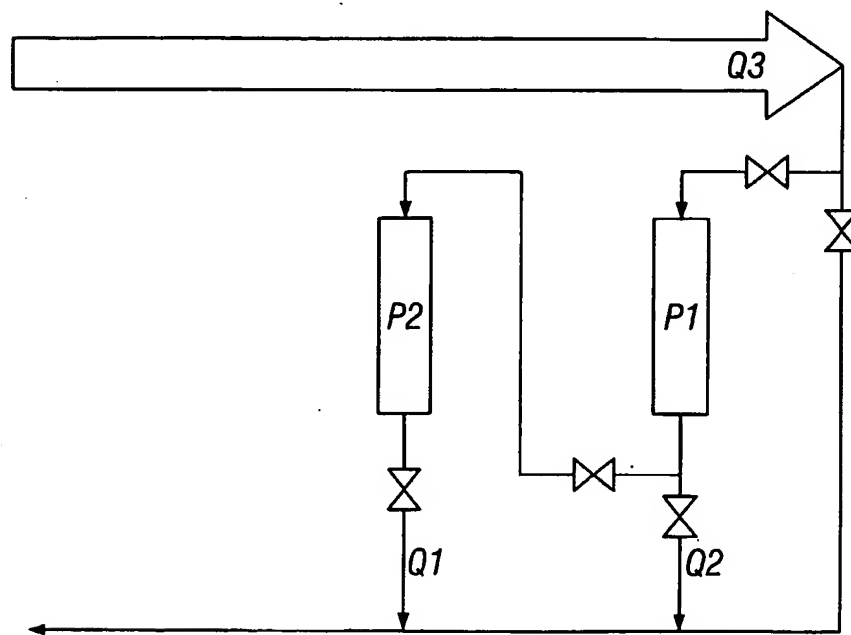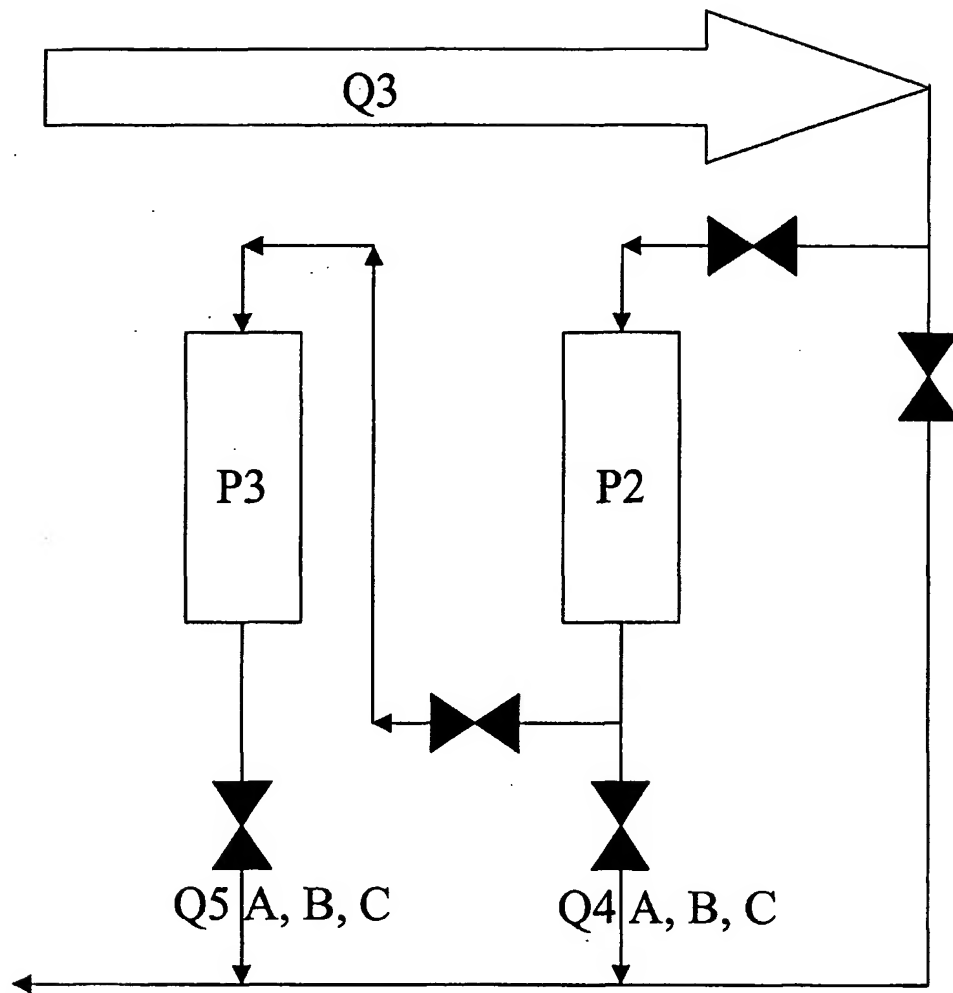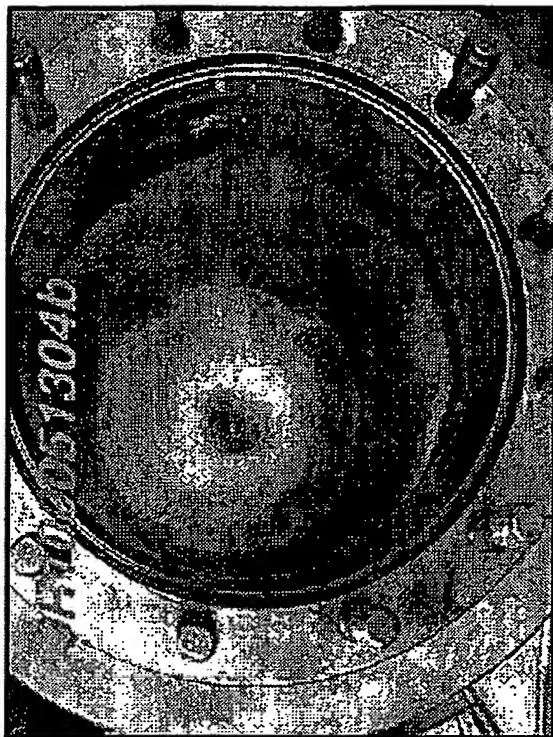2   a constrained geometry catalyst system.

FIG. 1

FIG. 2A

FIG. 2B

FIG. 3A

FIG. 3B

FIG. 3C

FIG. 3D

FIG. 4

FIG. 5

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   C08F10/00   C08F2/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 37510 A (UNION CARBIDE CHEM PLASTIC) 29 June 2000 (2000-06-29)	1,11
Y	page 20, line 27 -page 21, line 2 page 33, line 14 - line 16; claims	1
Y	WO 00 44798 A (XIE TUYU ;DU PONT (US)) 3 August 2000 (2000-08-03) page 7, line 9 - line 28; claims	1
A	US 5 326 855 A (KAHN HENRY) 5 July 1994 (1994-07-05) column 3, line 20 -column 4, line 21; claims	1
A	WO 97 32905 A (BOREALIS AS ;ALMQUIST VIDAR (NO); AASTAD TONE (NO); MELAAEN INGRID) 12 September 1997 (1997-09-12) page 5, line 18 - line 22; claims	1

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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Kaumann, E

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INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 65953 A (UNION CARBIDE CHEM PLASTIC) 23 December 1999 (1999-12-23) example 1 -----	1,10,14

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Information on patent family members

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(71) Applicant (for all designated States except US): DOW GLOBAL TECHNOLOGIES INC. [US/US]; Washington Street, 1790 Building, Midland, MI 48674 (US).

(72) Inventors; and
(75) Inventors/Applicants (for US only): NICASY, Ruddy

[BE/BE]; Molenwijk 42, B-2260 Westerlo (BE). GEMOETS, Frederik, E. [BE/BE]; t'Sween 7, B-2160 Wommelgem (BE). SCHOUTERDEN, Patrick, J. [BE/NL]; Statiestraat 199C, B-Wachtebeke 9185 (NL). VANDUN, Jozef, J. [BE/US]; 2911 Pecan Wood, Missouri City, TX 77459 (US).

(74) Agent: BAI, J., Benjamin; Jenkens & Gilchrist, 1100 Louisiana, Ste. 1800, Houston, TX 77002 (US).

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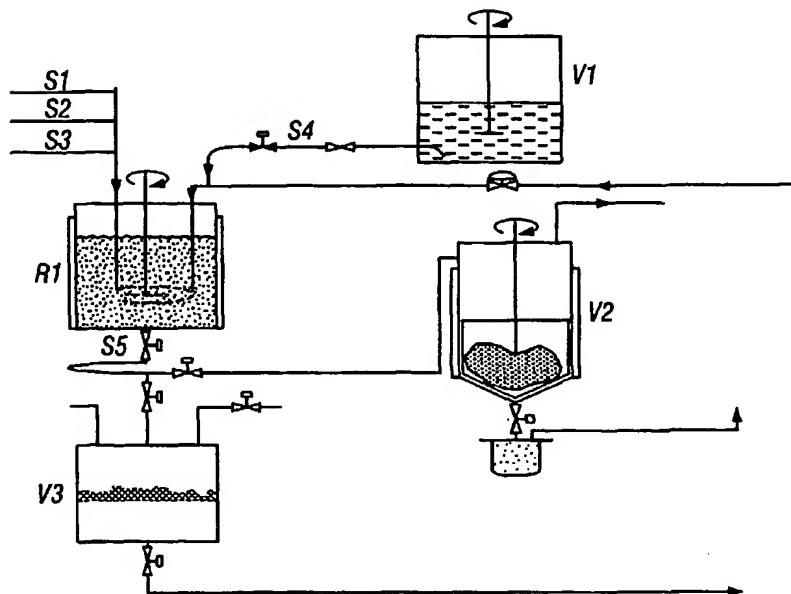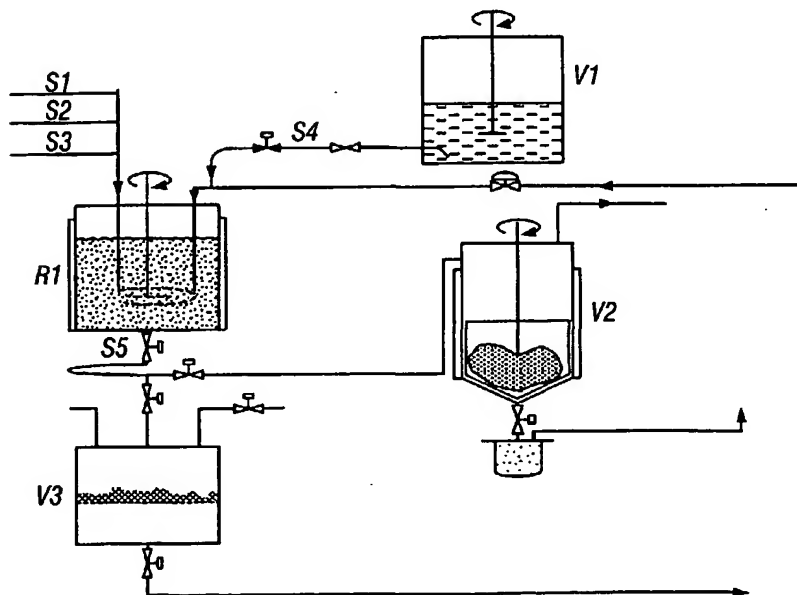
(57) Abstract: This invention pertains to a polymerization process for making ethylene polymers characterized as having reduced gels or reduced extraneous high molecular weight polymer fractions. The process comprises operating the polymerization at relatively high chain terminator agent to ethylene ratios in the post-reactor polymerization system, or providing higher purity ethylene feed, or avoiding cross-contamination between Ziegler-Natta or chromium catalyst systems and metallocene catalyst systems by using a critically clean procedure for catalyst vessels and transfer pipe. In preferred embodiments, some or all of the three process steps are utilized.

WO 2003/016362 A1

Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

1

ETHYLENE POLYMERIZATION PROCESS

FIELD OF THE INVENTION

This invention pertains to a polymerization process for making ethylene polymers characterized as having low or no gels, especially those due to extraneous high molecular weight polymer fractions.

BACKGROUND OF THE INVENTION

Polymerization processes that utilize Ziegler-Natta catalyst or chromium catalyst systems to manufacture ethylene polymers are well known in the art. With the introduction of new metallocene or single-site catalysts, these new catalysts are increasingly used to manufacture ethylene polymers via polymerization, such as gas phase or slurry polymerization processes. Polymerization experience with metallocene or single-site catalyst systems, when used in the same process equipment/configuration as with Ziegler-Natta catalysts or chromium catalysts) indicates that the new catalyst systems characteristically produce polymers with higher gel levels than Ziegler-Natta catalysts.

Gels that are observable in ethylene polymers are principally high molecular weight (HMW) polymer chains or fractions that are immiscible with the bulk polymer phase. While a few applications can tolerate gels, for the vast majority of polyethylene applications, gels are undesirable aesthetically or they adversely affect product performance.

It is known that polyethylene as produced still contains active catalyst residues. If the catalyst residues are not promptly deactivated, gels and/or extraneous HMW polymer fractions will result. As a result, catalyst kill agents (e.g. water, O_2, CO and CO_2) are routinely added to the polymer post-reactor in a process-finishing step.

Also, ethylene polymerization typically involves the use of chain terminating agents (e.g. hydrogen and isobutane) to control the product melt index or molecular weight to target. High levels of these agents reduce the molecular weight of the growing polymer by terminating chain growth or propagation. In practice, these agents are injected directly into the reactor wherein their levels are precisely controlled. But chain terminator concentration is not controlled to a high level in post-reactor equipment and vessels, as downstream of the reactor, polyethylene producers routinely vent these agents or at least do not maintain the higher levels previously existent in the reactor.

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In addition to being more prone to providing polymers with higher gel levels and/or higher quantities of extraneous HMW fractions, the use of metallocene or single-site catalysts have been found to result in substantially lower runtimes before the onset of reactor fouling and sheeting. Fouling and sheeting exists as polymer coatings on the reactor wall and

5   internal parts (e.g. stirrer blades and thermocouples). After the onset of fouling and sheeting, and as they continue to buildup, process efficiencies (e.g. catalyst efficiency, product yield and heat transfer) proportionally decrease which can cause a spiral or exponential effect. As fouling and sheeting continue, process efficiencies decrease until such time as continuing the polymerization becomes economically impractical and/or there is gross loss of process

10   control and the ability to produce products that are on-target.

While new forms of catalysts, such as the supported catalyst systems, offer marked improvement in runtime before the onset of fouling and sheeting, additional improvements are needed.

Further, given the wide availability of the new catalysts, ethylene polymer producers

15   desire the ability to use Ziegler-Natta catalysts or chromium catalysts in combination with metallocene or single-site catalysts in the same manufacturing facility to make different polymer products. Producers also desire the flexibility to use the different catalysts simultaneously for a single polymer product such as in a tandem polymerization with a different catalyst system being separately injected into different reactors. But experience

20   indicates that for facilities that utilize both catalyst systems even short runtimes before the onset of fouling and sheeting result relative to an equivalent facility dedicated exclusively to using new catalysts.

Accordingly, there is a need for a polymerization process that utilizes Ziegler-Natta and metallocene or single-site catalysts, either interchangeably or simultaneously, and

25   produces ethylene polymers characterized by reduced gel levels. There is also a need for a polymerization process that utilizes Ziegler-Natta and metallocene or single-site catalysts (either interchangeably or simultaneously), and exhibits improved runtimes before the onset of reactor fouling and sheeting.

SUMMARY OF THE INVENTION

30   The aforementioned needs are met by one or more aspects of the invention. In one aspect, the invention relates to a polymerization process for making a polymer, the polymer

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comprising ethylene and characterized as having low levels of gels or extraneous high molecular weight (HMW) polymer fractions or both, and the process comprising:

(I)   providing a polymerization system comprising:

    (a)   at least one by-passable purification unit,

    (b)   at least one catalyst feed vessel,

    (c)   at least one reactor, and

    (d)   post-reactor equipment and vessels, and

(II)   continuously polymerizing ethylene in the at least one reactor in the presence of an active catalyst which is continuously fed to the reactor, continuously transferring the polymerized ethylene downstream through to the post-reactor part of the system and:

    (a)   providing and maintaining a molar ratio of chain terminator to ethylene of from about 0.001 to about 0.5 throughout the post-reactor part of the polymerization system until all active catalyst is deactivated, or

    (b)   purifying the ethylene by directing the ethylene through the at least one purification unit before entry into the at least one reactor, or

    (c)   providing critically clean catalyst feed vessels

Additional aspects of the invention and advantages provided by various embodiments of the invention will become apparent with the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a slurry polymerization reactor system used in one embodiment of the invention.

FIG. 2A and FIG. 2B are schematics of feed gas purification systems used in embodiments of the invention.

FIG. 3 are photos showing the extent of reactor fouling and/or sheeting for various examples: 3A – Inventive Example 2; 3B – Inventive Example 3; 3C – Comparative Run 2A; and 3D – Comparative Run 2B.

FIG. 4 is a graph of the heat exchange coefficient across the reactor wall (U' values) vs. run time for various levels of ethylene purity.

FIG. 5 is a another graph of U' values vs. run time for various levels of ethylene purity.

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DETAILED DESCRIPTION OF THE INVENTION

Embodiments of the invention are based, in part, on one or more of the following discoveries. It has been found that polymerization that utilize metallocene or single-site catalyst systems possesses unique characteristics not typically known for Ziegler-Natta catalysts. Specifically, the chain terminator consumption rate is substantially higher for some metallocene or single-site catalysts relative to Ziegler-Natta catalysts. With regard to reactor fouling and sheeting, some metallocene or single-site catalysts are more sensitive to ethylene feed gas purity levels than Ziegler-Natta catalysts. It has been discovered that gels and/or extraneous HMW fractions can result from mixed catalyst systems due to cross-contamination.

Accordingly, a new polymerization process and a process system are provided. The process system comprises at least one catalyst feed vessel, at least one reactor, and post-reactor equipment and vessels. Optionally, at least one by-passable purification unit is also part of the process system. The polymerization process comprises (a) feeding the reactants and catalysts to the polymerization system; (b) continuously polymerizing monomers or comonomers (such as ethylene and 1-octene) in the reactor in the presence of an active catalyst which is continuously fed to the reactor; and (c) continuously transferring the polymer downstream to the post-reactor vessels. In addition, one or more of the following steps or acts are performed as desired: (1) providing a chain terminator in the post-reactor and maintaining a molar ratio of chain terminator to monomer or comonomer from about 0.001 to about 0.5 in the post-reactor until all active catalyst is deactivated; (2) purifying the monomer or comonomer by directing the monomer or comonomer through the at least one purification unit before entry into the at least one reactor; or (3) providing critically clean catalyst feed vessels. In preferred embodiments, all of the three steps or acts are employed.

The term "interpolymer" is used herein to indicate a copolymer, a terpolymer, a tetrapolymer, etc. That is, at least one other comonomer is polymerized with ethylene or other olefins to make an interpolymer. Suitable ethylene interpolymers which are produced from the reactor system comprise ethylene with at least one C_3-C_{20} α-olefin and/or C_4-C_{18} diolefin. Preferred comonomers include the one C_3-C_{20} α-olefins, especially propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, and 1-

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decene, more preferably 1-butene, 1-hexene, heptene and 1-octene. Most preferably, the ethylene interpolymer is a copolymer of ethylene and 1-butene.

In a preferred embodiment, the process system, as shown in Fig. 1, comprises a reactor R1, a catalyst feed vessel V1, a first post reactor vessel V2, and a second post reactor

5   vessel V3. A first monomer (S1), preferably ethylene, a chain terminating agent (S2), preferably hydrogen, and a solvent (S3), preferably butene, are fed to the reactor R1. The reactor R1 and the first post reactor vessel V2 are preferably jacketed and equipped with a means for agitation. The catalyst feed vessel V1 is also equipped with a means for agitation. The temperature of the reactor R1 ranges from about is from 20 to 115 °C, preferably from 50

10   to 105 °C. However, the upper limit of the polymerization temperature is a temperature which is highest among temperatures at which the ethylene copolymer produced can maintain substantially a powdery state. This temperature varies depending on the density of the ethylene copolymer produced and the type of diluent used. The pressure of the reactor R1 ranges from about 1 to about 100 atm, preferably from about 3 to about 30 atm. Catalyst (S4)

15   from the catalyst feed vessel V1 is also fed to the reactor R1.

The molar ratio of catalyst/cocatalyst employed preferably ranges from 1:10,000 to 100:1, more preferably from 1:5000 to 10:1, most preferably from 1:1000 to 1:1. Alumoxane, when used by itself as an activating cocatalyst, is generally employed in large quantity, generally at least 100 times the quantity of metal complex on a molar basis. The

20   remaining activating cocatalysts are generally employed in approximately equimolar quantity with the metal complex.

In general, the polymerization may be accomplished at conditions known in the art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from -50 to 250 °C, preferably 30 to 200 °C and pressures from atmospheric to 10,000 atmospheres.

25   Suspension, solution, slurry, gas phase, solid state powder polymerization or other process condition may be employed if desired. A support, especially silica, alumina, or a polymer (especially polytetrafluoroethylene or a polyolefin) may be employed, and desirably is employed when the catalysts are used in a gas phase or slurry polymerization process. Preferably, the support is passivated before the addition of the catalyst. Passivation

30   techniques are known in the art, and include treatment of the support with a passivating agent such as triethylaluminum. The support is preferably employed in an amount to provide a

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weight ratio of catalyst (based on metal):support from about 1:100,000 to about 1:10, more preferably from about 1:50,000 to about 1:20, and most preferably from about 1:10,000 to about 1:30. In most polymerization reactions, the molar ratio of catalyst:polymerizable compounds employed preferably is from about $10^{-12}{:}1$ to about $10^{-1}{:}1$, more preferably from

5   about $10^{-9}{:}1$ to about $10^{-5}{:}1$.

Suitable solvents for polymerization are inert liquids. Examples include, but are not limited to, straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; mixed aliphatic hydrocarbon solvents such as kerosene and ISOPAR (available from Exxon Chemicals), cyclic and alicyclic hydrocarbons

10   such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; perfluorinated hydrocarbons such as perfluorinated C_{4-10} alkanes, and the like, and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene, ethylbenzene and the like. Suitable solvents also include, but are not limited to, liquid olefins which may act as monomers or comonomers including ethylene, propylene, butadiene,

15   cyclopentene, 1-hexene, 1-hexane, 4-vinylcyclohexene, vinylcyclohexane, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene, styrene, divinylbenzene, allylbenzene, vinyltoluene (including all isomers alone or in admixture), and the like. Mixtures of the foregoing are also suitable.

The catalysts may be utilized in combination with at least one additional

20   homogeneous or heterogeneous polymerization catalyst in separate reactors connected in series or in parallel to prepare polymer blends having desirable properties. An example of such a process is disclosed in WO 94/00500, equivalent to U. S. Serial Number 07/904,770, as well as U. S. Serial Number 08/10958, filed January 29, 1993. The disclosures of the patent applications are incorporated by references herein in their entirety.

25   The catalyst system may be prepared as a homogeneous catalyst by addition of the requisite components to a solvent in which polymerization will be carried out by solution polymerization procedures. The catalyst system may also be prepared and employed as a heterogeneous catalyst by adsorbing the requisite components on a catalyst support material such as silica gel, alumina or other suitable inorganic support material. When prepared in

30   heterogeneous or supported form, it is preferred to use silica as the support material. The heterogeneous form of the catalyst system may be employed in a slurry polymerization. As a

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practical limitation, slurry polymerization takes place in liquid diluents in which the polymer product is substantially insoluble. Preferably, the diluent for slurry polymerization is one or more hydrocarbons with less than 5 carbon atoms. If desired, saturated hydrocarbons such as ethane, propane or butane may be used in whole or part as the diluent. Likewise the α-olefin

5   monomer or a mixture of different α-olefin monomers may be used in whole or part as the diluent. Most preferably, the major part of the diluent comprises at least the α-olefin monomer or monomers to be polymerized.

Solution polymerization conditions utilize a solvent for the respective components of the reaction. Preferred solvents include, but are not limited to, mineral oils and the various

10   hydrocarbons which are liquid at reaction temperatures and pressures. Illustrative examples of useful solvents include, but are not limited to, alkanes such as pentane, iso-pentane, hexane, heptane, octane and nonane, as well as mixtures of alkanes including kerosene and Isopar E™, available from Exxon Chemicals Inc.; cycloalkanes such as cyclopentane, cyclohexane, and methylcyclohexane; and aromatics such as benzene, toluene, xylenes,

15   ethylbenzene and diethylbenzene.

At all times, the individual ingredients, as well as the catalyst components, should be protected from oxygen and moisture. Therefore, the catalyst components and catalysts should be prepared and recovered in an oxygen and moisture free atmosphere. Preferably, therefore, the reactions are performed in the presence of a dry, inert gas such as, for example,

20   nitrogen or argon.

The polymerization may be carried out as a batch or a continuous polymerization process. A continuous process is preferred, in which event catalysts, solvent or diluent (if employed), and comonomers (or monomer) are continuously supplied to the reaction zone and polymer product continuously removed therefrom. The polymerization conditions for

25   manufacturing the interpolymers according to embodiments of the invention are generally those useful in the solution polymerization process, although the application is not limited thereto. Gas phase and slurry polymerization processes are also believed to be useful, provided the proper catalysts and polymerization conditions are employed.

In some embodiments, the polymerization is conducted in a continuous solution

30   polymerization system comprising two reactors connected in series or parallel. One or both reactors contain at least two catalysts which have a substantially similar comonomer

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incorporation capability but different molecular weight capability. In one reactor, a relatively
high molecular weight product (M_w from 100,000 to over 1,000,000, more preferably
200,000 to 1,000,000) is formed while in the second reactor a product of a relatively low
molecular weight (M_w 2,000 to 300,000) is formed. The final product is a mixture of the two

5   reactor effluents which are combined prior to devolatilization to result in a uniform mixing of
the two polymer products.   Such a dual reactor/dual catalyst process allows for the
preparation of products with tailored properties.   In one embodiment, the reactors are
connected in series, that is the effluent from the first reactor is charged to the second reactor
and fresh monomer, solvent and hydrogen is added to the second reactor. Reactor conditions

10   are adjusted such that the weight ratio of polymer produced in the first reactor to that
produced in the second reactor is from 20:80 to 80:20. In addition, the temperature of the
second reactor is controlled to produce the lower molecular weight product.   In one
embodiment, the second reactor in a series polymerization process contains a heterogeneous
Ziegler-Natta catalyst or chrome catalyst known in the art.   Examples of Ziegler-Natta

15   catalysts include, but are not limited to, titanium-based catalysts supported on $MgCl_2$, and
additionally comprise compounds of aluminum containing at least one aluminum-alkyl bond.
Suitable Ziegler-Natta catalysts and their preparation include, but are not limited to, those
disclosed in US Patent 4,612,300, US 4,330,646, and US 5,869,575. The disclosures of each
of these three patents are herein incorporated by reference.

20   Suitable catalysts include, but are not limited to, metallocene or single-site catalyst
systems. Preferably, the single-site or metallocene catalyst is a constrained geometry catalyst
system as described in WO 96/16092, WO 98/27119, and WO 96/28480, the disclosures of
which are incorporated herein by reference. More preferably, the metallocene or single-site
catalyst is supported using an inert material such as, for example, silica. More preferably, the

25   single-site or metallocene catalyst is reacted with a suitable co-catalyst (e.g., a boron-
containing compound or an alumoxane) which is bonded or fixed to the support in a prior
step such that the single-site or metallocene catalyst is immobilized to the extent that
substantially no soluble catalyst species is extracted from the support during polymerization,
most preferably the species are fixed or bonded such that there is substantially no extraction

30   when the solid catalyst system is boiled in toluene for 2 hours. Suitable single-site catalyst
systems for use in manufacturing the novel composition are also described in detail in US

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Patent Nos. 6,043,180 and 5,834,393, the disclosures of which are incorporated herein by reference. The supported catalyst systems used in polymerization make interpolymers with reverse comonomer distribution ("RCD"). The characteristics of these interpolymers, including RCD, are described in U.S. Provisional Application Serial No. 60/313,357, filed on
5   August 17, 2001, entitled "BIMODAL POLYETHYLENE COMPOSITION AND ARTICLE MADE THEREFROM," in names of Jozef J. Van Dun *et al.*, the disclosure of which is incorporated herein by reference.

During production, polymer (S5) is transferred to either the first post reactor vessel V2 or the second post reactor vessel V3. If polymer (S5) is transferred to the second post
10   reactor vessel V3, the unreacted monomers and diluent are removed. In an optional embodiment, conditions exist where the active catalyst can continue polymerizing under very low hydrogen ethylene ratio conditions. For the catalysts described above, hydrogen concentration drops faster than ethylene concentration due to the catalyst's intrinsic high consumption rate of hydrogen vs ethylene, and/or due to venting of the vessel since hydrogen
15   is preferentially vented vs ethylene due to the fact that hydrogen has a lower solubility. The post reactor vessels are not part of the reactor. They are separate from the reactor and have their own operating temperatures and pressures. The operating conditions of the post reactor vessels may be similar to the reactor or they may be different.

If polymer (S5) is transferred to the first post-reactor vessel V2, the terminator (S2)
20   concentration is relatively important in metallocene or single-site catalyst systems. It has been found that some of these catalysts have exceptionally high terminator reactivity/consumption rates relative to Ziegler-Natta or chromium catalysts. Accordingly, in preferred embodiments, the concentration for chain terminator agents in the post-reactor environment is kept in the range of about 0.001 to about 0.5 mole of terminator per mole of
25   ethylene. Below 0.001 mole terminator to mole ethylene, undesirable gel formation occurs and above 0.5 mole terminator to mole ethylene, undesirable oligomer formation occurs. More preferably, the range of from about 0.01 to about 0.4 or about 0.05 to about 0.2 mole of terminator to mole ethylene is maintained.

Chain terminators are also know as chain transfer agents or telogens which are used to
30   control the melt flow index in a polymerization process. Chain transfer involves the termination of growing polymer chains, thus limiting the ultimate molecular weight of the

polymer material. Chain transfer agents are typically hydrogen atom donors that will react with a growing polymer chain and stop the polymerization reaction of said chain. These agents can be of many different types, from saturated hydrocarbons or unsaturated hydrocarbons to aldehydes, ketones or alcohols. By controlling the concentration of the

5   selected chain transfer agent, one can control the length of polymer chains, and, hence, the weight average molecular weight, M_w. The melt flow index (MFI or I_2) of a polymer, which is related to M_w, is controlled in the same way.

After the donation of a hydrogen atom, the chain transfer agent forms a radical which can react with the monomers, or with already formed oligomers or polymers, to start a new

10   polymer chain. This means that any functional groups present in chain transfer agents, for instance, carbonyl groups of aldehydes and ketones, will be introduced in the polymer chains.

Any chain terminator agents known or presently unknown in the art may be used in embodiments of the invention. But preferred chain terminator agents include hydrogen, propylene and isobutane, with hydrogen being most preferred. The term "chain terminator

15   agent" is used interchangeably in the art with the terms "chain transfer agent" and "telogen".

A large number of chain transfer agents, for example propylene and 1-butene which have an olefinically unsaturated bond, can also be incorporated in the polymer chain, themselves, via a copolymerization reaction. This generally leads to the formation of short chain branching of respectively methyl and ethyl groups, which lowers the density of the

20   polymers obtained.

Another process for reducing the amount of HMW gels in the polymer product, is by using a critically clean catalyst feed vessel. By the term "critically clean catalyst feed vessel", it is meant that only disposable or one-time-use catalyst vessels are used or, when reusable catalyst vessels are used, prior to use they are cleaned by the following exemplary

25   procedure: as in ordinary cleaning, the contents of the catalyst vessel are drained and the vessel is rinsed with hexane or other diluents or solvents until it is visually free of solids. The catalyst vessel is then dried with N_2. In some embodiments, the catalyst vessel is filled with a mixture of hexane and isopropanol (concentration: 1:1 hexane/alcohol molar ratio) to a liquid level at least as high as the level of the previously contained catalyst system. The

30   alcohol/hexane mixture is then agitated for 2-3 hours and afterwards drained. The drained/empty vessel is then flushed with N_2 for 1 hour and then rinsed with hexane. The

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vessel is then filled with hexane and stirred for 1 hour and then drained and purged with N_2 for 1 hour. The hexane rinsing steps of stirring for 1 hour and purging with N_2 for 1 hour (or until dry) is then repeated. It should be understood that variations from the above procedure are acceptable so long as substantially similar results are achieved.

5   The critical cleaning procedure involves cleanup of the catalyst holding and feed vessels and catalyst feed lines to the reactors. It is effective in removing Ziegler-Natta catalyst or chromium catalyst residues and contaminants, and making the catalyst storage and feed lines and pumps suitable for use with a metallocene or single-site catalyst system. The process described herein is suitable for use in manufacturing olefin homopolymers or

10   interpolymers, especially ethylene homopolymers as well as ethylene interpolymers.

The cleaning method described above may be used during startup or when transitioning between different and/or incompatible catalysts. The catalysts are incompatible due to different reactivity ratios for molecular weight regulators and comonomers. They may detrimentally react with each other and reduce the activity of one or both catalysts. The

15   method may be used in gas phase, solution phase or slurry phase polymerization process systems. It may also be used in a two stage reactor system having two different catalysts.

Impurities in ethylene and possibly in the solvent feedstream can cause reactor fouling when using metallocene or single site catalysts. In-situ ethylene purification is preferably accomplished with the use of molecular sieve and/or activated alumina beds. As

20   shown in Fig. 2A, ethylene (Q3) from a pipeline is fed to a first purification unit P1. Alternatively, a second purification unit P2 may be in series or parallel with the first purification unit P1. The purification units, P1 and P2 may be bypassed by a series of valves (all of which are not shown). This gives the operator flexibility on the degree of purity (Q2 or Q3) to be sent to the reactor R1. The first purification unit P1 and the second purification

25   unit P2 are preferably filled with a molecular sieve or activated alumina bed for removing impurities from the ethylene. The molecular sieve may be of the zeolite type. The activated alumina may be of the gel, psuedoboehmite, gamma or bayerite type aluminas . In a preferred embodiment of the invention, in addition to in-situ purification of ethylene, process diluent and solvent as well as comonomer fed streams are also in-situ purified.

30   Process steps described above can be practiced in a gas phase, solution phase or slurry phase polymerization process system but they are particularly suitable for use in gas phase

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and slurry polymerization. These process steps can be used for a single-reactor polymerization system or a multiple reactor polymerization system either configured in series or in parallel. They can also be used in a multiple reactor system where there is separate fresh catalyst injection in each reactor as well as where there is fresh catalyst injection in the first reactor only.

In a multiple reactor polymerization system, post-reactor equipment and vessels exist after each reactor and intermediate to the next subsequent reactor. Thus, in a two reactor system, there are two post-reactor environment where the ratio of terminator to ethylene should be specifically controlled to provide a high level of terminator to avoid gel and extraneous HMW polymer fraction formation. Other suitable reactor systems are disclosed, for example, in WO 95/26370, WO 96/39450 and WO 97/32905, the disclosures of which are incorporated herein by reference in their entirety. The disclosed reactor systems may be used in embodiments of the invention with or without modifications.

By the term "extraneous high molecular weight polymer fraction" as used herein, it is meant that the HMW polymer fraction that is or was formed was not purposefully intended; that is, the fraction exists as an artifact of the intended bulk polymer. More particularly, the extraneous fraction was not formed in the reactor, it was formed in a post-reactor environment.

By the term "low gels" or "low extraneous HMW polymer fraction", as used herein, it is meant that the visual gel count on a 10 cm x 10 cm x 25 mm film fabricated at a melt temperature in the range of about 200 to about 212 °C will be less than about 300 gels/gram of film, preferably, less than or equal to about 250 gels/gram of film, more preferably, less than or equal to about 100 gels/gram of film and, most preferably, less than or equal to about 75 gels/gram of film.

The following examples are presented to illustrate various embodiments of the invention. They are not intended to be representative of all embodiments of the invention and should be not construed to limit the scope of the claimed invention as described here. All numbers described herein are approximate values and may vary within their accuracy ranges.

In the following illustrative examples, density was measured in accordance with ASTM D-792. Melt index measurements were performed according to ASTM D-1238, Condition 190°C/2.16 kilogram (kg) and Condition 190 °C/5 kg, and are known as I_2 and I_5,

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respectively. Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. Melt index is reported as g/10 minutes.

<div align="center">EXAMPLES</div>

5   Experiment 1

An experiment was conducted to determine the effect of terminator concentration in post-reactor environment on the gel level of corresponding products. For this experiment, a supported constrained geometry catalyst system was prepared following methods disclosed in WO 98/27119, Example 12. In a small, pilot polyethylene slurry polymerization facility, two

10   (2) sample taking points were devised as shown in FIG. 1: first post reactor vessel V2 and second post reactor vessel V3.

The first post reactor vessel V2 was operated at a low pressure (0.2 barg) at 70°C, and was continuously purged with N_2 and vented. In this way, the polymer slurry entering the first post reactor vessel V2 was dried. Because of the low pressure, N_2 purging and venting,

15   polymerization could not occur in the first post reactor vessel V2.

The second post reactor vessel V3 was designed to collect a slurry polymer sample directly from the reactor. The second post reactor vessel V3 had no insulation or cooling and thus the temperature at the device was lower than the reactor temperature. The pressure at the start of the experiment was about 2 to about 4 barg. During sampling, no venting took

20   place and the pressure increased to about 6 to about 7 bar. After sampling, the solvent was filtered from the polymer with N_2 pressure. After this step, the second post reactor vessel V3 was purged with N_2, then depressurized to atmospheric pressure. At these conditions, polymerization could continue. Second post reactor vessel V3 was then opened and the powder was collected in a drum wherein unreacted ethylene and hydrogen were permitted to

25   vent.

The samples were alternatively taken from the first post reactor vessel V2 (inventive example 1) and from the second post reactor vessel V3 (comparative run 1) during lined-out reactor conditions. During the sampling procedure, reactor was switched back and forth (about every 30 minutes) between the first post reactor vessel V2 and the second post reactor

30   vessel V3. In this way, sufficient and representative resins were sampled under exactly identical reactor conditions.

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All samples were produced under the same reactor conditions for homopolymer production: Reactor temperature = 70°C, Reactor pressure = 12 barg, hexane flow = 2800 g/hr. Additional process details are provide in Table 1 below.

TABLE 1

	Ethylene flow rate [g/h]	Hydrogen flow rate [Nl/h]	Vent flow rate [g/h]	Catalyst Yield [gPe/gTi]
Inv. Example 1A	823	0.8085	44.761	531,000
comparative run 1A	824	0.8084	44.917	531,000
Inv. Example 1B	834	0.856	45.28	669,000
comparative run 1B	884	0.9145	45.08	642,000

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The gel quality of resultant samples was measured by blowing film samples on a Haake film extruder (4.2 m long, thickness between 0.055 and 0.065 mm, layflat 75 mm, i.e. 10,000 in^2) at a melt temperature of about 210°C. The total visual gel count on a 10 by 10 cm film sample was then converted into gels/g and are reported below in Table 2.

10   TABLE 2

	Sampling point	I$_2$ (g/10 min)	Density (g/cm^3)	Gel count gels/gr
Inv. Example 1A	9	1.02	0.9610	179
Comparative run 1A	12	1.07	0.9615	499
Inv. Example 1B	9	0.86	0.9601	45
Comparative run 1B	12	0.73	0.9609	1,279

As shown in Table 2, the gel count of the inventive examples were substantially lower than the gel count for the comparative examples. As such, this experiment demonstrated that, under above conditions for the second post reactor vessel V3, unreacted ethylene and

15   hydrogen (the chain terminator agent) continued to react in a batch-wise mode wherein hydrogen was consumed much faster than the ethylene resulting in an imbalance which led to the formation of high molecular weight polymer and ultimately gels. Alternatively, by maintaining a high hydrogen level at the first post reactor vessel V2, substantially reduced levels of gels were obtained.

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Experiment 2

Another experiment was conducted to determine the effect of purification of the ethylene feed stream on the resistance to the onset of reactor fouling and sheeting. The

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polymerization system (FIG. 1) used in this experiment consisted of a single reactor R1 having a volume of 10 liter (no baffles) and equipped with a Lightnin A310 mixing blade running at about 750 rpm. All feed streams were fed through dip pipe legs in the liquid phase to allow intimate mixing. The reactor was operated at about 70 °C and a constant pressure of

5   about 12 bar. The reactor temperature was kept constant by jacket cooling and the pressure was kept constant by controlling the ethylene feed rate. The catalyst was pulsed into the main hexane diluent stream. The reactor level was kept at about 75 % of the total volume by discontinuously dumping the reactor content to the flash vessel. In this flash vessel (operating at a pressure of about 1.3 bar and a temperature of about 75 °C), the diluent and

10   unreacted monomers are evaporated and vented, resulting in a dry powder. The reactor was vented continuously to allow for gas analysis using an on-line gas chromatograph (GC). The GC provided an analysis of the reactor head space about every 6 minutes. The production rate was controlled by the catalyst flow and was calculated based on ethylene feed flow minus the vent flow through the vent. The diluent used was hexane.

15   The I_2 melt index of the polymer for the runs was controlled via hydrogen addition to the reactor, the density was controlled via comonomer addition to the reactor, and in all cases the comonomer was 1-butene, if present. Based on the polymer production and catalyst consumption, the catalyst efficiency was also calculated.

         The catalyst used in this experiment was a supported borate constrained geometry

20   catalyst system prepared as follows: Silica gel (948 grade available from Grace-Davidson) was dehydrated at an elevated temperature to a total volatiles of ca. about 3 wt. %. 24.71 kg of the resulting silica was slurried in 130 liters of dry hexane and then treated with 30.88 kg of a 1.21 M solution of triethylaluminum (TEA) in hexane. The slurry was filtered and washed with fresh, dry hexane (130 liters per wash) at ambient until the residual aluminum in

25   the wash was < 0.5 mmol/L. The solids were then isolated by filtration and dried under vacuum (~ 10 torr) at about 60 °C to a residual solvent level of less than or equal to about 1.0 wt. %. 1.5 moles of $[NHMe(C_{18\text{-}22}H_{37\text{-}45})_2]$ $[HOC_6H_4B(C_6F_5)_3]$, as 16.95 kg of a 10.1 wt. % solution in toluene, was diluted by addition of 9.61 liters (8.32 kg) toluene. This solution was allowed to agitate for about 10 minutes and then about 1.65 moles of TEA, as 0.88 liters

30   (0.76 kg), of a 1.87 M solution of TEA in toluene was added and the resulting solution allowed to mix for 15 minutes. Then the solid silica/TEA was added over approximately 30

16

minutes. On completion of the addition, the impregnated material was allowed to mix for about 60 minutes. With continuous agitation, about 195 liters (128.7 kg) of dry, fresh hexane at ambient was added to the solid and the resulting slurry was allowed to agitate for about 30 minutes. Then 1.2 moles of a constrained geometry catalyst, $(C_5Me_4SiMe_2N^tBu)Ti(\eta^4\text{-}1,3\text{-}$

5   pentadiene) (as 3.69 kg of a 0.223 M solution in heptane), was added and the slurry was mixed for about 2 hours. The solvent was removed from the slurry by filtration and the resulting solid washed four times with dry, fresh hexane at ambient and dried under vacuum to provide a free flowing powder.

In this experiment, single reactor runs were conducted at three (3) different ethylene

10   impurity levels to produce copolymer samples having a melt index I_2 of about 1.5 g/10 min and a density of about 0.940 g/cm^3. The first run was initiated with a pristine clean reactor and catalyst feed line. After each run, the reactor was disassembled, photographed and stripped clean to a pristine condition for the subsequent run.

The ethylene at different impurity levels was obtained by different levels of

15   purification. That is, ethylene purity as received from the pipeline contained the highest concentration of impurities and was designated Q3. Q3 ethylene was purified using an adsorption bed (P1) filled with 50% mol-sieve 3A and 50% Selexsorb™ COS material. With purification unit P1 in service, the ethylene quality was improved from level Q3 (before the purification unit P1) to quality Q2 (after the purification unit P1). Also, a second purification

20   unit (P2) was used in series with the P1 unit. Unit P2 consisted of a smaller size purification bed, filled with mol-sieve 3A. Ethylene passed through P1 and P2 was designated Q1 quality ethylene. FIG. 2A shows scheme for ethylene purification. The process conditions including total run time, GC gas analysis and product properties are shown in Table 3 for the various runs.

25   Table 3 indicates that when ethylene purity increases (i.e. improves), the run time increased. Also, catalyst productivity/efficiency substantially increased with increasing ethylene purity, and less fine particles were produced. But also, less lumps (defined as powder particles > 2 mm) were produced with increasing purity level. Table 4 provides the visual assessment of the various runs and FIGS. 3A - 3D show photos of the reactor taken

30   just after the various runs. These results illustrate that substantial reductions in the onset of reactor fouling and sheeting result with increased ethylene purity. In particular, Table 3

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indicates that the inventive process provides runtimes of greater than or equal to about 12 hours (preferably greater than or equal about 15 hours, more preferably greater than or equal to about 20 hours) per 600 pounds of produced polymer/hour per 10 liters of reactor volume before the onset of reactor fouling and sheeting.

5

TABLE 3

Example			Inv. Ex 2	Inv. Ex 3	Comp run 2A	Comp run 2B
Ethylene Purity			Q1	Q2	Q3	Q3
Reactor conditions	Reactor pressure	barg	12	12	12	12
	Reactor temperature	°C	70	70	70	70
	Catalyst flow	g cat/h	0.3915	0.6345	1.0695	1.023
	Hexane flow	g/h	2800	2800	2800	2800
	Hydrogen flow	Nl/h	0.80	0.75	0.62	0.67
	Ethylene flow	g/h	814	822	825	838
	Butene flow	g/h	39	40	41	42
	Reactor vent flow	g/h	234	209	239	222
	Production rate	g PE/h	580	613	586	616
Total run time		hrs	22	23	11	10
Catalyst Productivity		Kg PE/ g Ti	773	505	286	314
Reactor head space gas analysis	Nitrogen	Vol %	1.01	1.23	1.53	1.22
	Hydrogen	Vol %	0.22	0.23	0.21	0.21
	Ethylene	Vol %	92.18	90.63	92.09	91.71
	Ethane	Vol %	0.07	0.08	0.05	0.09
	Butene	Vol %	0.26	0.24	0.25	0.24
	Hexane	Vol %	3.85	3.35	3.51	3.03
Powder properties	Melt index I_2	g/10 min	1.53	1.05	0.66	0.48
	Density	g/cm³	0.9392	0.9366	0.935	0.9338
	Bulk Density	g/ cm³	0.305	0.299	0.318	0.269
	Powder D50	μm	493	428	347	-
	Fines	Wt %	2.62	3.79	17.05	-
	Lumps	Wt %	0	0	0.914	-

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TABLE 4

Example	Ethylene purity	Visual fouling evaluation	Fouling assessment
Inventive Example 2	Q1	Catalyst feed line showed some buildup but the reactor wall and internals were nearly pristine clean; only very limited hairy buildup. See Fig. 3A.	+
Inventive Example 3	Q2	Completely filled with powder. A thin, though film layer underneath all buildup at wall. See Fig. 3B.	-
Comparative Run 2A	Q3	Heavy buildup of powder, not powdery but firm. Underneath the buildup a thin an tough layer at the wall. See Fig. 3C.	-
Comparative Run 2B	Q3	Reactor filled with powder and very tough polymer material around the internal pipes, especially around the thermocouple. Dispersion pipe was completely surrounded and could not be removed by means . Around the impeller and at the bottom of the reactor wall there was heavy buildup. There was a thick film layer on the rest of the reactor wall. See Fig. 3D.	-

Experiment 3

In yet another experiment, the effect of conducting polymerization with critically

5   clean catalyst vessels and fed lines was investigated.   In this experiment, for inventive

example 4, the catalyst feed vessel (V1 in FIG. 1) was loaded with standard solid Ziegler-

Natta catalyst system at a concentration of about 3 g catalyst/kg hexane. The catalyst was

stored for about 1 week. After about 1 week, the contents of the catalyst vessel were drained

and the vessel was rinsed with hexane until it was visually free of solids. The catalyst vessel

10   was then dried with N_2. Subsequently, the vessel was cleaned as followed: the catalyst vessel

was filled with a mixture of hexane + isopropanol (concentration : 1:1 hexane/alcohol molar

ratio). The vessel was filled with the mixture such that the liquid level of alcohol/hexane

mixture was higher than the original catalyst/hexane slurry. The alcohol/hexane mixture was

then agitated at ambient for about 2 to about 3 hours. Afterwards, the alcohol/hexane mixture

15   was drained from the catalyst vessel and the vessel was flushed with N_2 for about 1 hour.

The catalyst vessel was then rinsed with hexane by filling the vessel with hexane and

agitating the hexane for about 1 hour, and then draining the vessel and purging it with N_2 for

about 1 hour. This hexane rinsing procedure was then repeated and provided a dry, critically

clean catalyst feed vessel.

20   The critically cleaned catalyst vessel was then loaded with a solid constrained

geometry catalyst system (conc. = 1.875 g catalyst/liter hexane) and stored overnight. After

this procedure, using the polymerization facility illustrated in FIG. 1, the solid metallocene catalyst was used to produce a single-reactor, butene copolymer having a melt index I_2 of about 1.5 g/10 min and a density of about 0.944 g/cm^3. After run, all transfer lines and vessels of the polymerization system were cleaned to avoid contamination of subsequent

5   runs.

For comparative run 3, the catalyst feed vessel was loaded with a standard solid Ziegler-Natta catalyst system at a concentration of about 3 g catalyst/kg hexane. The catalyst system was stored for about 1 week. After about 1 week, the contents of the catalyst vessel were drained and the vessel was rinsed with hexane until it was visibly free of solids. The

10   catalyst vessel was then dried with N_2 and loaded with the same constrained geometry catalyst system (concentration was about 25 g catalyst/ ml hexane) and stored overnight. After overnight storage, this catalyst system was used to produce a single-reactor, butene copolymer of having an I_2 melt index of about 1.5 g/10 min. and a density of about 0.944 g/cm^3.

15   The process conditions that were used for both Inventive Example 4 and comparative run 3 were as follows:

Reactor temperature = 70 °C,

reactor pressure = 12 barg,

gas composition: butene = 0.23 mole %, hydrogen = 0.2 mole %.

20   The resulting powder product from each run was collected and extruded on a Göttfert single screw extruder and then fabricated into cast film. Gels were measured on cast film by means of visual inspection. Table 5 provides the results from the gel evaluation as well as product properties.

TABLE 5

Example	I_2	density	gels
	g/10 min	g/cm^3	number/g
Inventive Example 4	1.33	0.9435	256
Comparative Run 3	1.84	0.9426	883

25

The results in Table 5 clearly indicate that polymerization using a critically clean catalyst feed vessel can dramatically reduce the gel level of the resultant ethylene polymer.

20

Experiment 4

In still another series of tests, ethylene with different impurity concentrations obtained by different levels of purification is used to produce polyethylene in a slurry miniplant. Single reactor experiments were conducted to produce a homopolymer polyethylene with a melt index $I_2 = 150$ g/10 min from different purity levels of an ethylene feed stream. The purification unit P1 was replaced (swapped) during operation at varying time intervals. The purification system is similar to the one described in Fig. 2A and is illustrated in Fig. 2B.

Ethylene used comes from the pipeline (pipeline quality). In the following examples, this ethylene is called Q3 quality ethylene and contains the highest concentration of impurities. The ethylene can be purified by using an adsorption bed (P2) filled with either Molesieve 3A (from UOP), Selexsorb CD (activated alumina from Alcoa) or Selexsorb COS (activated alumina from Alcoa). When this purification unit (P2) is put into service, the ethylene quality is improved from level Q3 (Before the purification unit P2) to quality Q4A (when P2 is filled with Molesieve 3A), Q4B (when P2 is filled with Selexsorb CD) or Q4C (when P2 is filled with Selexsorb COS) after the purification unit P2. A second purification unit (P3) can be used, in series with the P2 unit filled. Unit P3 consists of a same size purification bed as P2, filled with Selexsorb CD or Selexsorb COS. In this way, the purity of ethylene with quality Q4A can be improved to quality Q5A (with molesieve 3A in P2 and Selexsorb CD in P3) or to quality Q5B (with molesieve 3A in P2 and Selexsorb COS in P3). Also the ethylene with quality Q4B can be improved to quality Q5C (with Selexsorb CD in P2 and Selexsorb COS in P3).

The catalyst used was a solid supported borate CGC catalyst as described above for Example 2. The experiments were continued until stable operation was no longer possible.

TABLE 6

Experiment			4A	4B	5	6
Ethylene Purity			Q1	Q1	Q2	Q1B
Reactor conditions	Reactor pressure	barg	12	12	12	12
	Reactor temperature	°C	70	70	70	70
	Catalyst flow	g cat/h	1.512	1.92		
	Hexane flow	g/h	3500	3500	3500	3500
	Hydrogen flow	Nl/h	7.735	7.81	5.7	9.5
	Ethylene flow	g/h	1682	1669	1713	1670
	Reactor vent flow	Nl/h	45	45	45	45
	Production rate	g PE/h	1474	1476	1500	1450
Total run time		Hrs	12.5	11	4.75	25.5

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Catalyst Productivity		Kg PE/ g Ti	510	396	-	450
Reactor head space	Nitrogen	Vol %	2.87	2.76	3.92	2.24
	Hydrogen	Vol %	1.09	1.09	1.05	1.26
	Ethylene	Vol %	88.49	87.7	86.6	92.2
	Ethane	Vol %	0.29	0.30	0.34	0.65
	Hexane	Vol %	2.89	3.01	2.82	3.24
Powder properties	Melt index I2	g/10 min	137	128	-	-
	Bulk Density	g/ cm^3	0.434	0.433	-	-
	Powder D50	µm	551	544	-	-

When the ethylene purification is improved by repeatedly switching the purification bed, the run time is drastically increased. The U'-value was monitored during the runs. The U'-value is the heat transfer coefficient across the reactor wall and is defined by the heat

5   transferred through the reactor wall divided by the temperature difference over the reactor wall and is expressed in units [kJ/K/hr]. The U'-value is a measure of the fouling on the wall of the reactor.

Figure 4 shows the U'-value of the reactor wall during the 4 experiments. The vertical lines show the times at which the P1 purification units have been swapped in experiment 6.

10   The U'-value plots in this graph clearly show that the fouling rate is lower with better purification.

Example 5

In another series of tests, ethylene treated with different purification adsorbents is used to produce polyethylene in a slurry miniplant. Single reactor experiments were

15   conducted to produce a homopolymer polyethylene with a melt index I$_2$ = 150 g/10 min. Experiments with different ethylene purification adsorbents were performed to determine the influence of ethylene purification adsorbents on the reactor fouling performance.

As shown in Fig. 2B, ethylene is used that comes from the pipeline (pipeline quality). In this example, this is called Q3 quality ethylene and contains the highest concentration of

20   impurities. The ethylene can be purified by using an adsorption bed (P1) filled with either Molesieve 3A (from UOP), Selexsorb CD (activated alumina from Alcoa) or Selexsorb COS (activated alumina from Alcoa). When this purification unit (P1) is put into service, the ethylene quality is improved from level Q3 (Before the purification unit P1) to quality Q4A (when P1 is filled with Molesieve 3A), Q4B (when P1 is filled with Selexsorb CD) or Q4C

25   (when P1 is filled with Selexsorb COS) after the purification unit P1.

22

A second purification unit (P2) can be used, in series with the P1 unit filled. Unit P2 consists of a same size purification bed as P1, filled with Selexsorb CD or Selexsorb COS. In this way, the purity of ethylene with quality Q4A can be improved to quality Q5A (with molesieve 3A in P1 and Selexsorb CD in P2) or to quality Q5B (with molesieve 3A in P1 and Selexsorb COS in P2). Also the ethylene with quality Q4B can be improved to quality Q5C (with Selexsorb CD in P1 and Selexsorb COS in P2).

In all these experiments freshly regenerated beds were used at the beginning of each experiment. Purification beds were not swapped during an experiment. The catalyst used was a solid supported borate CGC catalyst as described above for Example 2.

The experiments 7 (Q4A), 10 (Q5A) and 11 (Q5B) have run until yield and U'value have dropped to 70% of the original value or unless it was impossible to run the reactor without large temperature deviations from the reactor temperature setpoint. Experiments 8 (Q4B) and 9 (Q4C) have only been allowed to run for 19 hr before shutdown. Experiment 12 (Q5C) was shutdown after 57 hr due to operational issues that were not caused by reactor operation. This run had prematurely failed.

TABLE 7

Experiment			7	8	9	10	11	12
Ethylene Purity			Q4A	Q4B	Q4C	Q5A	Q5B	Q5C
Reactor conditions	Reactor pressure	barg	12	12	12	12	12	12
	Reactor temperature	°C	70	70	70	70	70	70
	Catalyst flow	g cat/h	1.74	1.44	1.38	1.5	1.404	1.512
	Hexane flow	g/h	3500	3500	3500	3500	3500	3500
	Hydrogen flow	Nl/h	8.36	8.7	8.26	8.3	8.1	7.8
	Ethylene flow	g/h	1688	1754	1723	1724	1681	1762
	Reactor vent flow	g/h	150	150	150	150	150	150
	Production rate	g PE/h	1465	1530	1500	1501	1458	1536
Total run time		Hrs	22	19	19	72	72	57
Catalyst Productivity		Kg PE/ g Ti	445	550	575	533	534	530
Reactor head space	Nitrogen	Vol %	2.03	1.49	1.47	1.66	2.07	1.41
	Hydrogen	Vol %	1.11	1.1	1.11	1.09	1.09	1.02
	Ethylene	Vol %	93.01	93.21	93.95	93.65	93.68	92.55
	Ethane	Vol %	0.48	0.36	0.35	0.4	0.4	0.32
	Hexane	Vol %	3.04	3.19	3.37	3.26	3.36	3.95
Powder properties	Melt index I2	g/10 min	144	167	141	153	150	146
	Bulk Density	g/ cm³	0.403	0.43	0.44	0.385	0.391	0.384
	Powder D50	µm	523	550	553	540	532	553

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When the ethylene purification is improved by using multiple and different purification beds, the run time is drastically increased. The U'-value was monitored during the runs. The U'-value is the heat transfer coefficient across the reactor wall and is defined by the heat transferred through the reactor wall divided by the temperature difference over the

5   reactor wall and is expressed in units [kJ/K/hr]. The U'-value is a measure of the fouling on the wall of the reactor. Fig. 5 shows the U'-value of the reactor wall during the above described experiments.

As demonstrated above, embodiments of the invention provide a polymerization process and system which produces polymers with less gels or extraneous high molecular

10   weight polymer fractions. The reactor system, when operated in accordance with embodiments of the invention, exhibits a reduced level of reactor fouling and/or sheeting. As a result, the runtime and thus the efficiency of the reactor system has increased. Other advantages are apparent to those skilled in the art.

While the invention has been described with respect to a limited number of

15   embodiments, the specific features of one embodiment should not be attributed to other embodiments of the invention. No single embodiment is representative of all aspects of the inventions. Moreover, variations and modifications therefrom exist. For example, while the production of ethylene interpolymers is preferred use of the processes described herein, the processes can be applied to manufacture any polymer. The processes are described in terms

20   of one or more steps or acts, it should be understood that the process can be practiced in any order or sequence of the acts or steps. Although particle-form polymerization is the preferred use of the processes, they may also be employed for non-particle-form polymerization, such as continuous solution polymerization, with or without modifications. Finally, equivalent catalysts to metallocene or constrained geometry catalysts may be used instead. The

25   appended claims intend to cover all such variations and modifications as falling within the scope of the invention.

What is claimed is:

24

1   1.   A polymerization process for making a polymer, the polymer comprising ethylene and
2   characterized as having low levels of gels, and the process comprising:
3   (I)   providing a polymerization system comprising:
4   (a)   at least one by-passable purification unit,
5   (b)   at least one catalyst feed vessel,
6   (c)   at least one reactor, and
7   (d)   post-reactor equipment and vessels which are separate from the at least
8   one reactor, and
9   (II)   continuously polymerizing ethylene and optional comonomers in the at least
10 one reactor in the presence of an active catalyst which is continuously fed to the reactor,
11 continuously transferring the polymerized ethylene and the optional comonomers from the
12 reactor to the post-reactor equipment and vessels and:
13   (a)   providing a chain terminator in the post-reactor equipment and vessels
14   and maintaining a molar ratio of chain terminator to ethylene of from
15   about 0.001 to about 0.5 in the post-reactor until all active catalyst is
16   deactivated, or
17   (b)   purifying the ethylene by directing the ethylene through the at least
18   one purification unit before entry into the at least one reactor, or
19   (c)   providing critically clean catalyst feed vessels, or
20   (d)   any combination of (a)-(c).

1   2.   The process of Claim 1 wherein the ethylene polymer is characterized as
2   having a visual gel count of less than or equal to 250 gels per gram of film.

1   3.   The process of Claim 1 wherein the polymerization system comprising at least
2   two ethylene purification units.

1   4.   The process of Claim 3 wherein the two ethylene purification units comprise
2   molecular sieve beds.

25

1   5.   The process of Claim 1 wherein the process is characterized as providing a

2   runtime of greater than or equal to 15 hours per 600 pounds of produced polymer/hour per 10

3   liters of reactor volume before the onset of reactor fouling and sheeting.

1   6.   The process of Claim 1 wherein the critically clean catalyst vessel is provided

2   by the use of a disposable or single-use catalysts vessel.

1   7.   The process of Claim 1 wherein the critically clean catalyst vessel is provided

2   by using the cleaning procedure comprising a polar compound.

1   8.   The process of Claim 7 wherein the polar compound is selected from alcohol

2   or water.

1   9.   The process of Claim 1 wherein the chain terminator agent is hydrogen.

1   10.   The process of Claim 1 wherein the chain terminator agent is maintained in

2   the post reactor system at a level in the range of from about 0.01 to about 0.4 mole of

3   terminator to mole ethylene.

1   . 11.   The ethylene polymer obtainable by the process of Claim 1.

1   12.   The ethylene polymer of Claim 11 wherein the polymer is an interpolymer.

1   13.   The ethylene polymer of Claim 11 wherein the polymer is manufactured using

2   a supported metallocene catalyst system.

1   14.   The ethylene polymer of Claim 13 wherein the metallocene catalyst system is

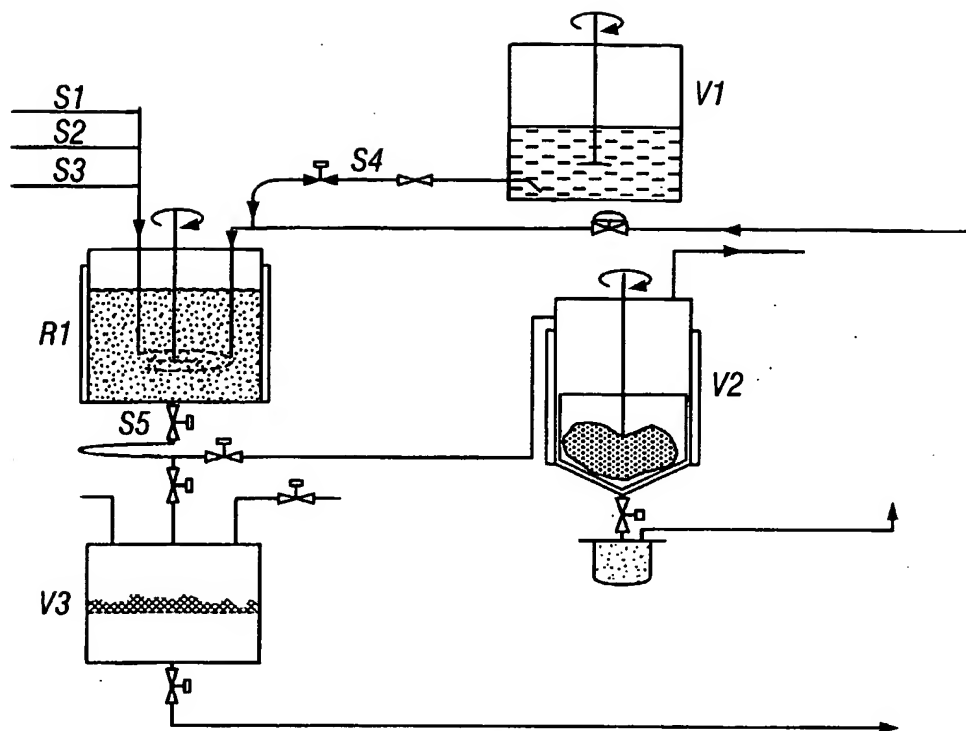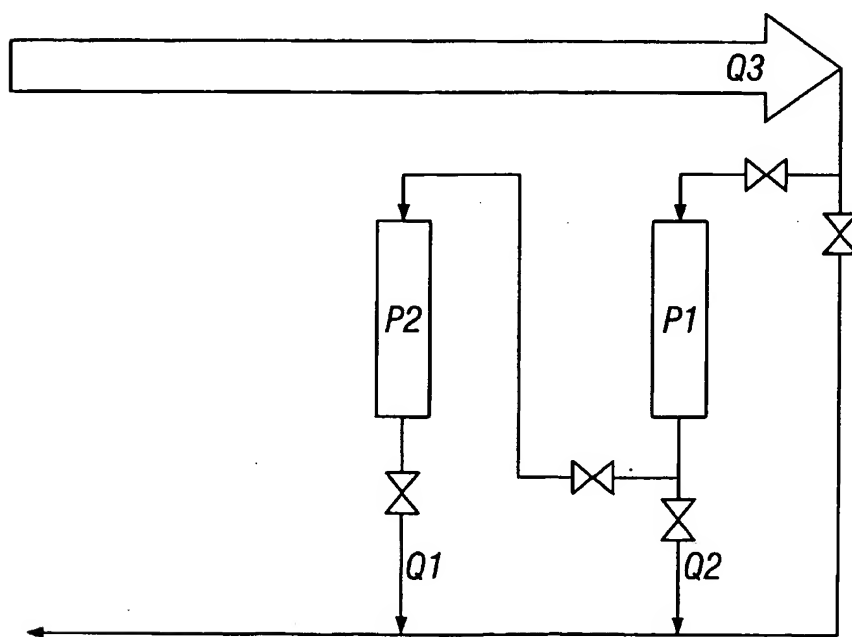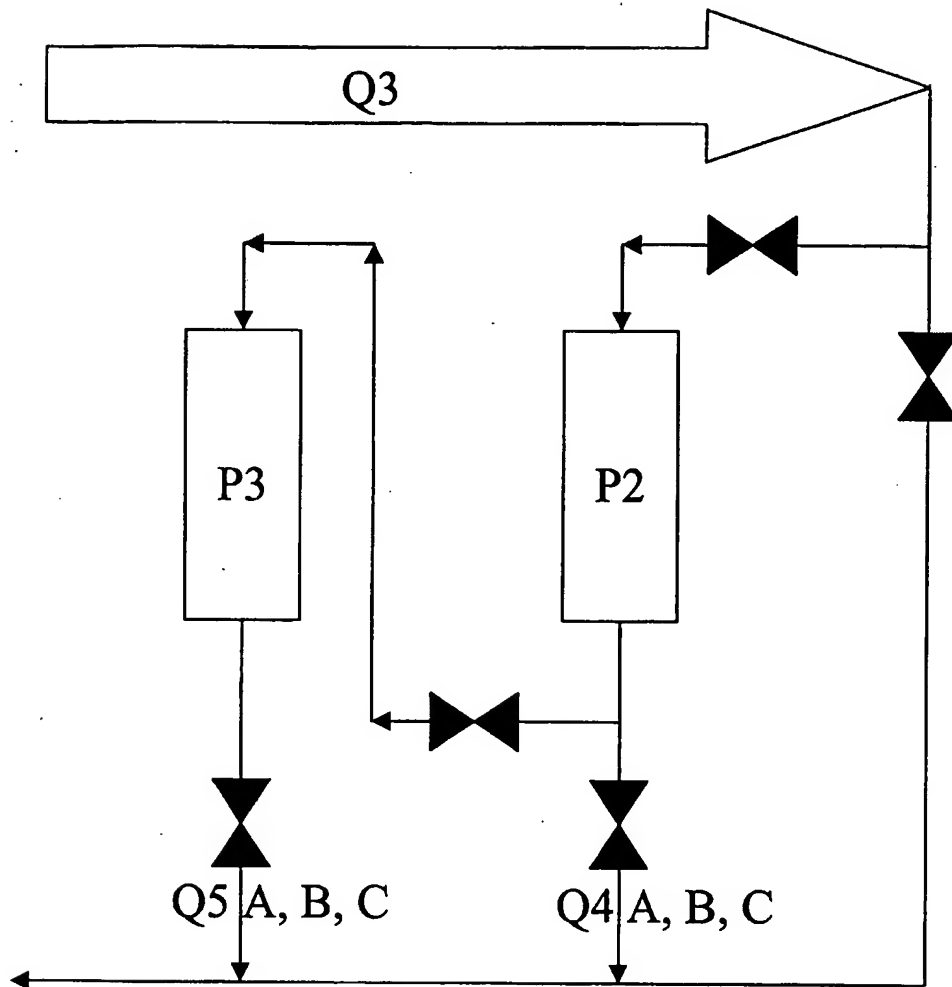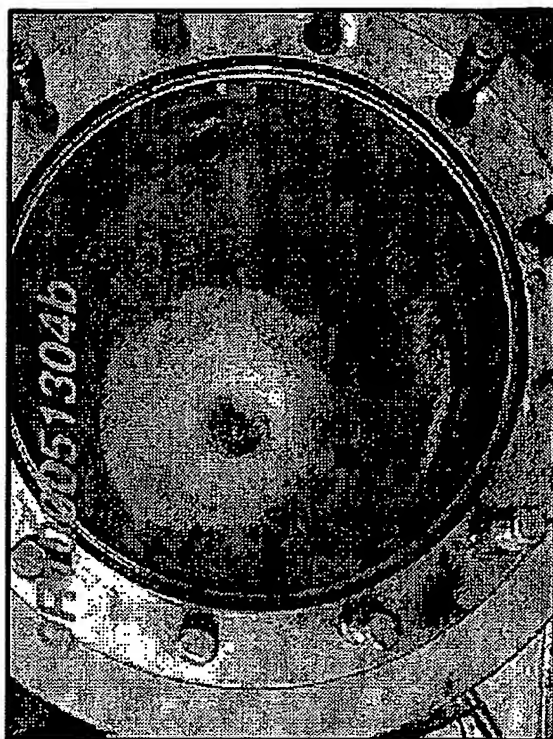2   a constrained geometry catalyst system.
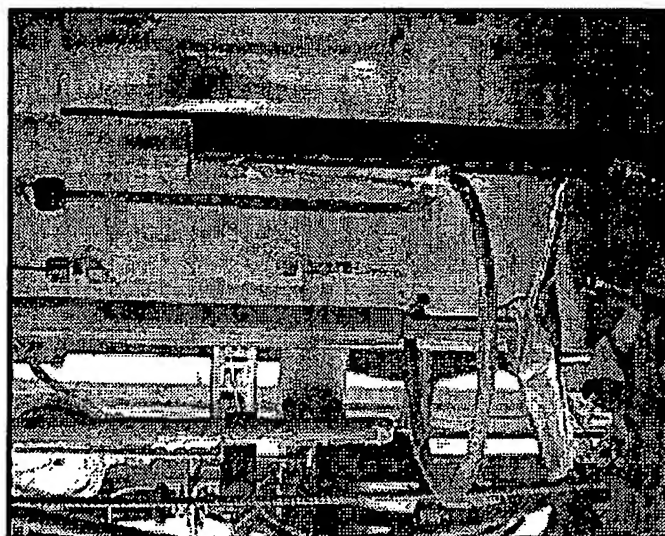
FIG. 1

FIG. 2A

Q3
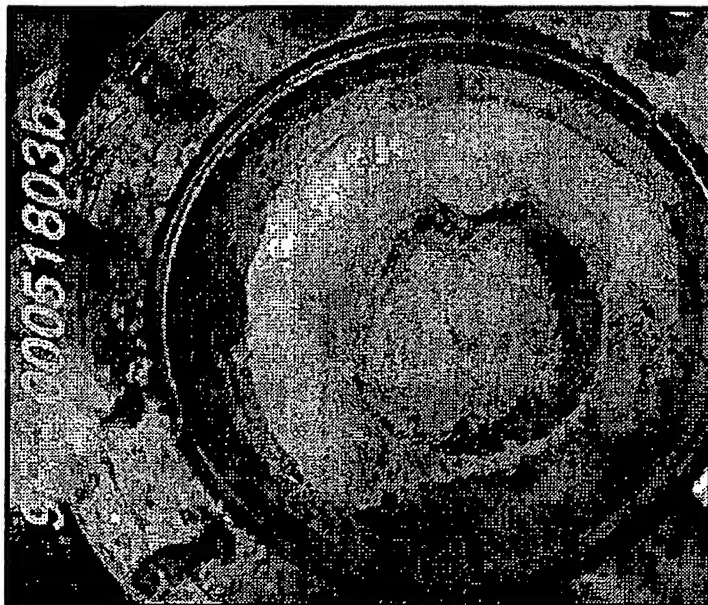
P3

P2

Q5 A, B, C   Q4 A, B, C

FIG. 2B

FIG. 3A

FIG. 3B

FIG. 3C

FIG. 3D

FIG. 4

FIG. 5

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   C08F10/00   C08F2/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7   C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 37510 A (UNION CARBIDE CHEM PLASTIC) 29 June 2000 (2000-06-29)	1,11
Y	page 20, line 27 -page 21, line 2 page 33, line 14 - line 16; claims	1
Y	WO 00 44798 A (XIE TUYU ;DU PONT (US)) 3 August 2000 (2000-08-03) page 7, line 9 - line 28; claims	1
A	US 5 326 855 A (KAHN HENRY) 5 July 1994 (1994-07-05) column 3, line 20 -column 4, line 21; claims	1
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-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 November 2002	12/12/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Kaumann, E

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 65953 A (UNION CARBIDE CHEM PLASTIC) 23 December 1999 (1999-12-23) example 1	1,10,14

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

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